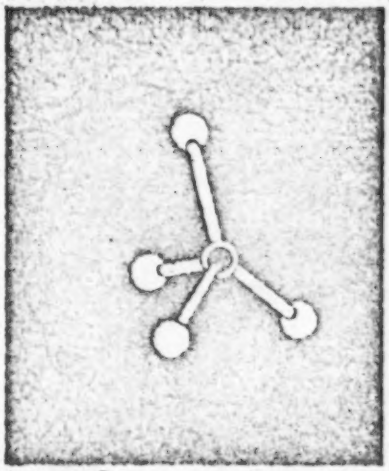
Journal of Structural Chemistry

Vol. 2 No. 5

Volume 2, Number 5

September-October, 1961



JOURNAL OF STRUCTURAL CHEMISTRY

ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ / ZHURNAL STRUKTURNOI KHIMII

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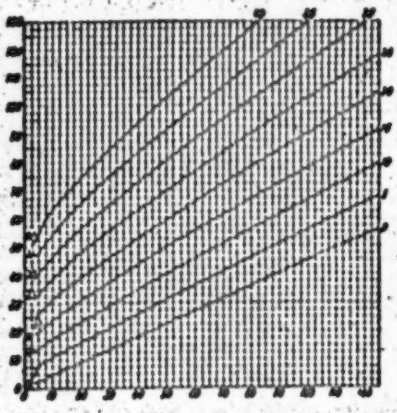

TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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International atomic weights (Appendix)

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JOURNAL OF

STRUCTURAL CHEMISTRY

A translation of ZHURNAL STRUKTURNOI KHIMII,

a publication of the Academy of Sciences of the USSR

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227 West 17th Street, New York 11, N. Y.

Volume 2, No. 5 September-October, 1961

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Annual Subscription: $80 **Single Issue: $20** **Single Article: $12.50**

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ERRATA

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p. 439, equation (1) should read :

$$0.326x + 0.438y - 0.839z = 0.$$

SCIENTIFIC ACHIEVEMENTS –
TO SERVE THE BUILDING OF COMMUNIST SOCIETY

Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 531-532, September-October, 1961

The Soviet Union has entered upon a new stage in its development – the stage of extensive building of a communist society. No social economic formation has ever needed science as much as the communist society does. Never before has there been a regime which opens up such wide horizons for the development of science, such limitless possibilities for scientists, as the social regime of our country. The development of science in the USSR has long ceased to be the concern of scientists alone. The strength of Soviet science lies in the unity of scientists with the whole people.

The prophetic words of V. I. Lenin, uttered in the spring of 1920, have been fulfilled. He wrote: "The cooperation of the representatives of science and the workers, only such cooperation will be capable of destroying all the oppression of poverty, sickness, and dirt. will be achieved. No force of darkness can withstand the union of the representatives of science and technology" (Works, Vol. 30, p. 376). One remarkable achievement of this union was the creation of the fabulous space ships "Vostok-1" and "Vostok-2," in which the glorious sons of the Soviet people, Yu. A. Gagarin and G. S. Titov took the first steps in the conquest of space. This historic achievement of all our people and our advanced science was celebrated by rewards to a large group of scientists, engineers, and workmen, the conquerors of space. The Soviet people received the high esteem of their work with great satisfaction.

The extensive building of communism confronts scientists with more and more new and ever more complex tasks. In the words of N. S. Khrushchev: "The creation of the material and technical basis of communism requires that science should flourish and demands the active participation of scientists in the solution of problems involved in further all-around development of the productive forces of our country."

These words were the keynote of the entire work of the All-Union Conference of Scientific Workers, convened on June 12, 1961 in the Kremlin by the Central Committee of the CPSU and the Council of Ministers of the USSR. At this conference Soviet scientists unanimously approved the decision of the Party and Government, "On measures for improving the coordination of scientific research in the country and in the activity of the Academy of Sciences of the USSR."

The documents of the Conference bear witness to the enormous range of development of science and scientific institutions, and to the ever-growing need for science in industry. They also express the concern of the Party and the Government for the development of science at this new stage. The address by the President of the Academy of Sciences of the USSR M. V. Keldysh, and speeches by participants at the Conference, indicated the most effective paths for further development of science, improvement of coordination, and increase of the role of science in all branches of industry and in agriculture.

After the reorganization, the Academy of Sciences of the USSR will be able to intensify work in the cardinal directions of science and greatly to extend the relative significance of fundamental theoretical research. In his address to the Conference, member of the Presidium of the Central Committee of the CPSU, first Deputy Chairman of the Council of Ministers of the USSR A. N. Kosygin said: "...We fully understand and support the scientists doing theoretical work on problems, the practical application of which is a matter for the relatively distant future. Science must be ahead of practice; it must look ahead not only to tomorrow but to the day after."

Soviet chemistry is confronted with enormous tasks. It is sufficient to mention that, in accordance with the Seven-Year Plan, capital investment in the chemical industry will exceed 10 billion rubles. This is more than five times the investment during the previous seven years. During the same period the volume of production of the whole chemical industry will be more than tripled. All Soviet scientists will find a place and will take worthy part in the fulfillment of this great plan. They must develop the most promising processes for synthesis of new materials.

Structural chemistry, as one of the youngest and most vigorously developing branches of chemical science, has an especially large contribution to make to the development of chemistry, because, in our day, the theoretical principles of the atomic structure of gases, liquids, and solids are being more and more widely applied in practice. The growth of the semiconductor industry, the polymer industry, and the production of superhard and heat-resisting

alloys has conferred special importance, in particular to the chemistry of solids, the progress of which is inseparably linked with the solution of problems in structural chemistry.

The editorial board of this journal will assist in every way the publication of scientific research in this field, and will help to raise even higher the level of the work published.

The publication of the project of the new Party program, which, for the first time in history, presents the task of building a communist society as the direct practical task for the immediate future, has aroused enormous joy and a surge of creative strength in all our people and in Soviet scientists. The project of the program states that application of science is becoming the decisive factor in the mighty growth of the productive forces of society, that the development of science and application of its achievements in the national economy will, in the future, be a matter of special concern for the Party.

On the eve of the 22nd Congress of the CPSU, our scientists, together with the whole Soviet people, labor purposefully and make their contribution to the building of communist society. They are seeking new ways of intesifying the development of scientific research, revealing the potentialities for further growth of scientific achievements, improving the coordination of work of the scientific institutions, universities, and technical colleges. Our scientists await the 22nd Congress with great creative enthusiasm. They devote their new achievements to it and there can be no doubt that, inspired by its decisions, they will raise our science even higher, to a level worthy of a communist society.

M. V. LOMONOSOV AND THE PROBLEM OF THE STRUCTURE OF MATTER

(ON THE 250th ANNIVERSARY OF HIS BIRTH)

L. L. Potkov

Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 533-541, September-October, 1961

Paraphrasing Tuytchev's well-known words about Pushkin, we can say that Russian science will never forget Lomonosov as its first love. Although we are separated by two centuries from his day and science has gone very far from the problems, methods of investigation, and hence the potentialities of the first half of the 18th century, the works of Lomonosov are often reprinted and quite recently a 10-volume complete collection of his works (with parallel texts) was produced. Lomonosov's work was studied throughout the whole of the 19th century and during the present century; special interest in them arose in the middle of the 1800's (100th anniversary of his death), at the end of that century (in connection with the 150th anniversary of Lomonosov's foundation of the first scientific chemical laboratory in Russia), and at the beginning of the 20th century (the 200th anniversary of his birth). The study of Lomonosov's work developed very widely during the Soviet era, and especially after the Great Patriotic War. As science developed, so analysis of his contribution to the treasury of knowledge deepened and views on this contribution were revised.

The range of Lomonosov's interests and talents, unusual even for the epoch of the Encyclopedists, which was vividly portrayed in Pushkin's picturesque account, was beyond the comprehension of certain historians. For example, one of them, F. Hoefer, in the list of chemists of the middle of the 18th century given in his History of Chemistry, wrote: "Among Russians who achieved fame as chemists we may mention Mikhail Lomonosov, who should not be confused with the poet of the same name" [1, p. 367].

Lomonosov's work on chemistry and other natural and technical sciences was based on the atomistic system which he had developed very extensively. In some aspects, this system was a further development of the atomistic concepts of P. Gassendi, R. Boyle, I. Newton, H. Huygens, and R. Descartes. In his consideration of other problems Lomonosov rejected the ideas of his predecessors. Lomonosov worked on his system throughout his life, starting in 1738. "After I had read Boyle, I was possessed by a passionate desire to investigate the minutest particles. I pondered upon them for 18 years" wrote Lomonosov in 1756 [4, p. 241]. Although he never succeeded in writing a comprehensive monograph on atomistics, many of his writings and notes contain a wealth of ideas which together constituted a very important advance in the progress of science, and especially of physics, chemistry, and philosophy.

Among Lomonosov's atomistic ideas, a special place is occupied by thoughts associated in one way or another with the problem of the structure of matter. "The basis of the properties of natural bodies," he wrote, "must be sought in the qualities of the corpuscles* and in the manner of their mutual disposition..." [2, p. 25]. These ideas are scattered among nearly all his writings on chemistry, physics, geology, and mineralogy. Although these concepts altered with the years and the statements associated with them are, in most cases, of a fragmentary character, we can isolate from them certain ideas which gradually supplemented each other and ultimately formed an integral system. We shall attempt to reproduce this system here.

Lomonosov rightly emphasized the guiding importance of scientific theory in chemical investigation and was sharp in his condemnation of empiricists. In one of his works he asked the reader to wait patiently for completion of his whole system. He stressed that this future work of his is especially necessary to those "who, turning with praise to chemical practice alone, dare not raise their heads above the coals and ashes lest they should consider as vain and futile the searches for the causes and nature of the primary particles which constitute matter, from which the colors and other properties of sensible** bodies originate. A knowledge of primary particles is needed in physics

*i.e., molecules. – L. P.

**Lomonosov called objects which could be perceived by our senses "sensible bodies," whereas those which could not be perceived (atoms and molecules) he termed "insensible." – L. P.

inasmuch as primary particles themselves are needed to compose sensible bodies. For what purpose have so many experiments in chemistry and physics been conducted ? For what purpose have great men labored and performed dangerous tests? Was it only to collect a great multitude of different things and matters in a disorderly heap and then to look and marvel at their numbers without pondering their disposition and order?" [4, p. 342].

Lomonosov said that hypotheses must be advanced in order to understand the meaning of experiments and to perform them correctly and in order to obtain results important for science. "This is the sole road by which the greatest men reached the discovery of the most important truths. This is a sort of impulse which makes them capable of attaining knowledge which the minds of the lowly who grovel in the dust can never aspire to" [4, p. 231]. However, Lomonosov gave serious warnings to avoid all unjustified conjectures which are not in any way connected either with the previous development of science or with experimental knowledge. Yet writings about natural science in the 17th and 18th centuries were full of just such conjectures about natural philosophy. Lomonosov wrote: "I rate one experiment higher than a thousand opinions created only by the imagination. But I deem it necessary to coordinate experiments with the needs of physics" [2, p. 125]. Here, by physics Lomonosov meant natural science as a whole. Thus, "the true chemist must be a theoretician and a practitioner" [2, p. 71].

Lomonosov based his ideas of natural science and philosophy on the concept of matter, which "is that which composes a body and on which its nature depends" [2, p. 173]. Elsewhere he says that "matter is something extended, divisible into insensible and mutually impenetrable particles" [2, p. 106]. However, this primary matter is not something homogeneous; on the contrary, it consists of diverse "principles." Lomonosov shows the way whereby experiment can lead to this concept of matter.

A "mixed body" (in the 17th and 18th centuries these words covered the concepts both of a chemical compound and of a mixture; see below) cannot be analyzed indefinitely – there must be components in which "unlike bodies cannot be separated from each other by any chemical operations or distinguished by reasoning; therefore, bodies of this kind we describe...as principles" [3, p. 487; see also 2, p. 143]. Elsewhere, Lomonosov refers to a "principle" as "a body consisting of the same kind of corpuscles" [2, p. 81]. Thus, Lomonosov gives the definition of a chemical element in accordance with Boyle, who regarded it as the limit of decomposition of a substance into its constituents. However, Boyle rejected the objectivity of qualitative differences and attributed the origin of various properties of matter to conditions. "The one and the same parcel of the universal matter may, by various alternations and contextures, be brought to deserve the name sometimes of a sulphureous and sometimes of a terrene, or aqueous body" [6, p. 64].

Boyle asserted that form and not composition determines the properties of a substance. Since the properties of metals depend only on different disposition ("texture") of the corpuscles, it follows that transmutation of metals is possible. Hence, wrote Boyle, "it is not absurd to doubt whether, for ought has been prov'd, there be a necessity to admit any elements or hypostatical principles at all" [6, p. 186 et seq.]. The cause of these doubts was Boyle's inability to correlate his proposed concepts with the concrete forms of atoms, because analytical data on chemical composition were lacking at that time (the first information was obtained only at the end of the 18th century). This also accounts for the contradictory nature of Lomonosov's views – he often used alchemical concepts alongside of Boyle's ideas [see 4, p. 333; 5, p. 601]. At the same time he opposed the idea of the alchemical "elements" – peripatetic concepts, and especially "fire," which was supported by Boyle [see 3, pp. 45-49, etc.].

Lomonosov frequently referred to the origin, changes, and destruction of animals, plants, and inorganic substances as evidence of motion of the particles composing them [see 2, pp. 73, 147, 159]. In accordance with the level of science of that time, Lomonosov reduced all forms of motion to one – mechanical motion; he therefore formulated the problem of studying the motion of insensible particles by means of mechanics; in his opinion, the solution of this problem would make chemistry a science [see 2, pp. 73 and 75].

When insensible particles move with direct contact, cohesion arises between them which "offers resistance to the force disrupting their bond" [2, p. 267]. Lomonosov discusses in detail the possible causes of cohesion. First, he emphasizes that neither the size nor the inertia force of the particles is the sole cause of this cohesion. He considered that gravity cannot cause cohesion of particles. Motion alone is likewise insufficient for cohesion to arise; it occurs only when a special fluid "insensible" batter fills the gaps between the particles of the substance. "It, like fluids susceptible to observation, like air and water...pressed on the corpuscles in opposing directions and was the cause of the cohesion observed in them" [2, p. 47; see also 4, p. 383].

The long-known empirical fact that not all bodies interact when brought into contact is explained by Lomonosov in terms of a special mechanism proposed by him, the most important element of which is the particle form. Whereas Gassendi, Boyle, and other atomists of the 17th and 18th centuries attempted to explain the diversity of natural bodies in terms of various geometrical forms of the particles which were believed to be joined by hooks, wedges, rings, etc., Lomonosov rejected these hypotheses on the principle of the maximum simplicity. Lomonosov

wrote: "I have perceived during frequent consideration during twenty years, and as a result of experiments, that Nature eases the task of those who search into her mysteries by contenting herself with sphericity alone" [4, p. 387; see also 4, pp. 222-223]. Lomonosov returns to sphericity of particles in many of his writings, attempts to prove it by various experimental observations, and draws up a whole program for such investigations [2, pp. 141-143]. In his opinion, sphericity, in particular, follows "from the invariability of cohesion...from the assumption...by liquids of such configuration; angular corpuscles would coalesce into angular forms..." [2, p. 143]. Since insensible particles rotate, they must inevitably be spherical [4, pp. 389 to 391].

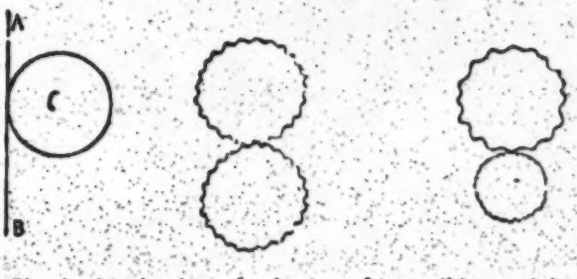

Fig. 1. Mechanism of cohesion of insensible particles [3, p. 229]: compatible particles in the middle, incompatible on the right.

However, particle surfaces may differ, and particles consisting of one or several "principles" have either like or unlike surfaces. In the former case, particles unite when they come together; in the latter they do not. If the unevennesses on the surfaces of the particles are equal in size and similarly arranged, the particles may join them like wheels by cogs. Lomonosov therefore defines "particles which join with each other as compatible, and those which do not join and do not move together as incompatible" [4, p. 329]; (see Fig. 1).*

He attached very great important to this phenomenon, because, in his view, "one body cannot act directly upon another without touching it" [3, p. 119]. Lomonosov believed that "combination [explains] colors, tastes, odors, all sensations, all hitherto unexplained sensible effects. And all that is chemical" [4, p. 239, see also 3, p. 231]. One of the fundamental postulates of Lomonosov's disseration "On the Origin and Nature of Saltpeter" is concerned with the combination phenomenon. "Between homogeneous principles and mixed bodies containing a large amount of one principle there is a certain mutual correspondence by virtue of which they combine with each other more readily than with unlike bodies and, penetrating into each other, join to each other. This combination differs from simple cohesion as only particles brought into contact are bonded by means of the latter" [3, p. 227].

Thus, cohesion of combining atoms forms molecules. The views of Lomonosov on the concept of the molecules were a considerable advance over the corresponding views of Gassendi, Boyle, and Newton. Gassendi considered that atoms differ only in size, shape, and weight, as matter everywhere is exactly the same; here Gassendi was a true follower of Epicurus. But, unlike the Greek philosopher, Gassendi considered that atoms join to form minute concretions (concreticulae) or small masses (moleculae) which subsequently become progressively larger and more complex, and form larger and larger bodies. The properties of a body depend only on the combination and disposition of atoms in the molecule and of molecules in the body [7, p. 140].

Following Gassendi, Boyle considered that the properties of bodies are derived mainly from the motion, shape, and disposition of small particles in them [6, p. 175]. We have already referred to Boyle's views on the origins of the properties of bodies. Here we may add that in Boyle's view, "concretions" or "clusters" (i.e., molecules) of complex bodies consist directly of "clusters" of simple substances (chemical elements), so that, according to Boyle, the atom was in a sense lost from view. With regard to Newton's atomistics, here, in accordance with the requirements of optics (and it is in this connection that Newton considered atomic and molecular structure most fully [see 8, section 31]), the main attention was devoted to the complexity of the structure of particles [9, p. 715; 10], and Newton did not accept the concept of a chemical element in Boyle's sense.

Lomonosov's approach to the problem of the relationship between the significance of atoms and molecules was much more correct than that of his predecessors. He wrote: "A corpuscle is a collection of elements** joined together in one small mass (corpusculam est elementorum in unam massulam congeries)" [2, p. 78]. In his definition, "corpuscles are of the same kind if they consist of equal numbers of the same elements joined in the same way [2, p. 79]; we can see the definition of an element and of its molecules. Elsewhere Lomonosov wrote of an element that "particles or molecules of water...[consist] of combinations of its atoms..." [3, pp. 111-113] (water at that time was regarded as an element). He puts forward the following argument to prove the existence of elements. "By

*All the drawings are by Lomonosov himself.

**Here and in similar instances Lomonosov uses the term element as a synonym of atom. — L. P.

chemical analysis it can be shown that mixed bodies contain similar* simple bodies, from which it is evident that mixed bodies also consist of similar simple bodies" [2, p. 307].

The characteristics of complex substances are defined by Lomonosov as follows: "Corpuscles are unlike when their elements are different and are joined in different ways or in different numbers; upon this the infinite diversity of bodies depends" [2, p. 81].

Lomonosov, like his predecessors, did not draw sharp distinctions between chemical compounds, mixtures, and solutions, and termed them mixed bodies. However, in some cases he gives a fairly precise definition of the concept of a chemical compound. "A mixed body is that which consists of two or several different principles so joined to each other that each of its individual corpuscles bears the same relation to the parts of the principles of which it consists as the whole mixed body does to the whole separate principles" [2, p. 81].

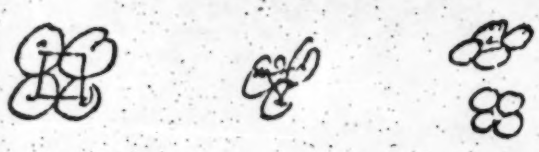

Fig. 2. Diagram showing disposition of elements within corpuscles [4, p. 311]; left – square; middle – triangular; right – square and rhombic.

Lomonosov held that certain properties of mixed bodies depend on "different joining of the particles, because no change of mixing in chemistry can ensue without a change in the joining of the particles" [3, p. 489]. Moreover, according to his views, a change in a body can occur only when something is added to it or taken from it, or when the disposition of its parts changes [2, p. 393]. Therefore, Lomonosov held that one of the most important tasks of chemistry is to seek causes of mutual "union," whereby all the primary particles "combine in the composition of bodies and from which all the differences of solidity and fluidity, fluidity and softness, flexibility and fragility originate" [3, p. 355; see also 4, pp. 397 and 399].

"Hitherto," stated Lomonosov in his Word in Favor of Chemistry, "chemistry has revealed only the matters which compose mixed bodies, and not each particle separately... But if ever this mystery is solved, chemistry will truly be the leader of the discovery... By...the example of [mathematics], in discussing the innumerable and diverse changes which chemistry presents by mixing and separation of various substances the intellect must attain the measure, motion, and position of the primary particles, hidden by their immeasurable smallness, which compose mixed bodies" [3, p. 353]. Later, Lomonosov emphasized that the lover of nature who wishes to comprehend the primary particles must "discern" especially those "properties and changes" which chemistry reveals when "it joins separated and scattered particles from solutions into solid parts and forms them into different figures." The nature lover must "turn to the cautious and perceptive geometry to find when [chemistry] changes solid bodies into liquid and liquid into solid, and separates and joins different kinds of matter, consult the precise and ingenious science of mechanics, and when it produces different colors by the confluence of liquids he must investigate them by penetrating optics" [3, pp. 353-354].

Thus, the Russian scientist correlated the properties of substances with their structure; his views on the structure of salts and stones are of interest in this respect [11].

We know that before Lomonosov's time this relationship was sought by P. Gassendi, R. Boyle, R. Hooke, H. Huygens, I. Newton, and others. In carrying out his investigations of crystals, N. Steno also wrote that the relationships found by him are of significance to the atomists. Lomonosov utilized some of the views advanced by the above-named scientists, developed them, carried out observations, and reached a number of most important conclusions. Moreover, he attempted to justify experimentally those of his ideas which originated from atomistic concepts only.

Lomonosov wrote that the form of crystals, which can be studied by our senses, enables us to draw conclusions about the form of corpuscles [2, pp. 107 and 151]. He considered that particles in solids and liquids are arranged thus:

*"A similar body is one, any sensible part of which is like any other 'sensible part' with respect to its particular qualities [qualitatis particulares], i.e., it...has the same density, color, cohesion of physical parts, etc." [2, p. 299].

[2, p. 131], and attempted to compute mathematically the difference between these forms of corpuscle packing. Evidently it was in terms of such packing that he wanted to explain why the shape of metal particles detached from a lump appears square or rhombic [2, pp. 117, 131, 153]. "When the spherical particles are arranged so that in each tetrad the centers are at the corners of the square abcd, and two tetrads fit exactly into a cube, then the disposition is square. If the lines *l* m, mn, nl form a triangle, I call this disposition triangular, wherein the figure formed by four particles is rhombic... Between the square and triangular dispositions there are almost innumerable intermediate dispositions, where the particles a and d move away from each other, while b and c come closer together, and vice versa..." [4, pp. 311-313] (see Fig. 2).

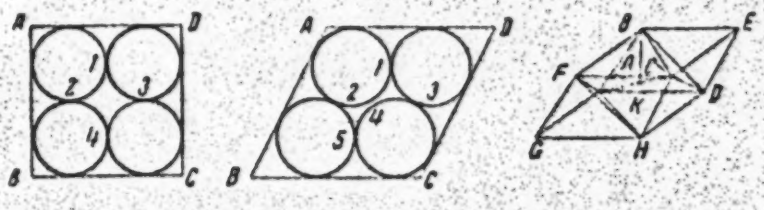

Fig. 3. Arrangement of elements within corpuscles [4, p. 403]; disposition in one row – square (left), rhombic (middle); spatial disposition – rhombohedron (right).

Elsewhere, Lomonosov developed this idea more fully: "...Let us consider the different positions of the particles, which can safely be assumed spherical in the light of the foregoing (see Fig. 3). Four spherical particles in close position and contact may be included in an equilateral rhombic figure, while in the most extended disposition and in contact they must be in a cubic figure" [4, p. 399].

From the above reasoning Lomonosov concluded that simple bodies, i.e., those consisting of like particles and not containing extraneous matter in the interstices, can expand and contract without disturbance of the union between the particles. At the same time, extraneous matter such as air may prevent the closest, i.e., rhombic, union and, according to Lomonosov, the degree of compression (in other words, the packing density) depends on the amount of extraneous matter between the particles of the substance. "...Since there must be twelve contacts between eight particles in the cubic position and eighteen in the rhombic, it is not surprising that when the particles change from the first to the second they acquire strong union of hardness, having lost the [connecting] fluid [fluidus], the more so the stronger the six contacts and unions are formed" [4, p. 401]. It follows that, for spheres, the cubic packing is the loosest and the rhombic packing the closest. This is illustrated by Lomonosov's drawing (Fig. 3), where a spatial picture of rhombic packing of sphere is shown on the right (the lines join the centers of the spheres).

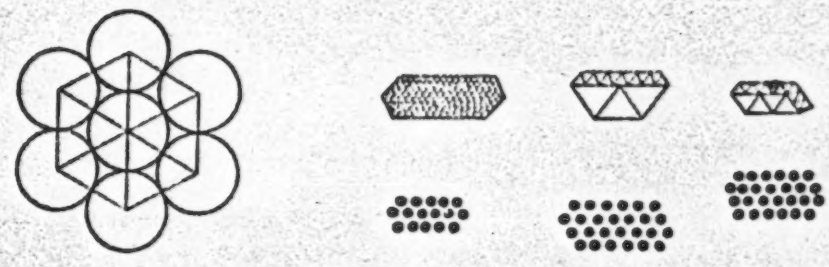

Fig. 4. Schematic diagram of the crystal structure of saltpeter [3, pp. 274-275].

All of Lomonosov's ideas on the structure of crystals received especially vivid expression in his investigation of saltpeter. He wrote: "If we suppose that...particles of saltpeter have a spherical form, to which the minutest natural bodies accumulated in heaps [in comulum congestal], mostly tend, it is easy to explain why saltpeter grows in six-sided crystals... Suppose that six corpuscles are so arranged near each other that the straight lines joining their centers form equilateral triangles (Fig. 4): we then have a figure bounded by six lines, like the section of a prism formed by saltpeter. The saltpeter particles, arranged in this manner in almost infinite numbers, form crystalline prisms of saltpeter, often admittedly with unequal sides, but the sides are always parallel and correspond to the postulated arrangement as the diagrams (Fig. 4) show... Moreover, this conjecture is confirmed in three ways: 1) in

this explanation the form of the particles is not assumed to be the same as the form of the saltpeter crystals themselves... 2) the corners of the saltpeter crystals correspond to the supposed arrangement of the particles, since usually each is 120°; 3) on the basis of our hypothesis it is easy to explain other kinds of crystals, such as cubic crystals of common salt, by assuming that the salt particles are so arranged that the lines passing through their centers form squares [3, pp. 273-275].

As early as the beginning of the 1740's, Lomonosov wrote that in crystals "opposite angles and opposite sides are equal, and the diagonals correspond to circles so arranged" [2, p. 107]. In the above citation on the structure of saltpeter crystals he states that the angles are equal in all the crystals because of the equal arrangement of the particles. Thus, Lomonosov strove to use the hypothesis of the internal structure of crystals for explaining the constancy of crystal angles.

Lomonosov planned an extensive program for investigation of crystals, but apart from the work cited above only a few notes concerned with measurements of crystal angles have reached us. Lomonosov wrote: "Crystals have a prismatic six-sided shape, wherein they are very similar to saltpeter crystals. Sometimes they are also cubic, and they are usually colored or semitransparent and are softer than six-sided ones" [5, p. 420]. "Finally, limestones,* and above all, precious stones, follow in their origin the geometrical laws of angles and planes and are predominant in hardness and transparency. Many of them are generated in a rhombic shape, having two angles of 60° and two of 120°, which I measured in a certain large uncut diamond and other transparent stones. Others are six-sided parallelepipeds, whereby they much correspond to grains of different salts and are no doubt deposited similarly..." [5,p. 599].

As V. I. Vernadskii [13] points out, many scientists, beginning with J. Kepler (1615), drew attention to the constancy of crystal angles. After him W. Davisson and P. Gassendi wrote on this subject in the first half of the 17th century. During the second half of the 17th century N. Steno first stated the law of constant angles for all crystalline substances. The same law, but with respect to Iceland spar only, was stated by E. Bartolinus, and with respect to gypsum by Leeuwenhoek. At the end of the 17th century, R. Boyle and (more lucidly) Guglielmini, demonstrated the applicability of this law to crystallization of salts and attempted to classify the simple forms. The views of H. Huygens on the homogeneity of crystal structure drew greater attention.

It follows that measurement of crystal angles was far from a new thing, as were attempts to correlate the structure of crystals with atomistic concepts. Despite this, Lomonosov's views in this field are of very great interest. He tried to explain the regularity of crystal structures, not in terms of supposed regularities of corpuscles (which would require experimental justification impossible at that time), but on purely geometrical considerations – the principles of packing of spheres (as already noted, Lomonosov assumed that corpuscles are spherical). No one before Lomonosov had this idea, which can only now be valued to the full [14, p. 8].

Thus, the works of Lomonosov contain many remarkable ideas on the structure of matter; these ideas have been developed during the subsequent progress both of chemistry and of crystallography. Some of these ideas were ahead of the concepts of that time by decades and even by a century.

The path of Lomonosov's researches, originating from the idea that atoms of different "principles" enter in integral numbers into chemical compounds, led directly to the discovery of the law of multiple proportions, i.e., to the union of philosophical atomistics with the results of chemical investigations of matter. It was only the lack of experimental data on the compositions of at least a few gases and salts, which were obtained only during the last third of the 18th century (i.e., after Lomonosov's death), which prevented the Russian scientist from making this discovery [15].

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*Limestone, calcite. – L.P.

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ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF THE ANTIMONY (III) OXIDE MOLECULE

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 542-544, September-October, 1961
Original article submitted September 29, 1960

The geometry of the antimonous oxide molecule was investigated by vapor-phase electron diffraction with the aid of refined techniques.

It was found to be a dimeric molecule of the composition Sb_4O_6, analogous in structure to oxides of other group V elements.

Electron-diffraction studies of the oxides of trivalent phosphorus and arsenic (sesquioxides) showed [1-3] that vapors of these compounds contain dimeric molecules of the E_4O_6 type.* An attempt [1] to obtain electron-diffraction patterns of antimony sesquioxide vapor was not successful. Determination of experimental data on the structure of the antimony sesquioxide molecule is of interest because such data to some extent complete the investigations of the molecular structure of similar sesquioxides of elements of group V of the periodic system, and therefore should reveal the laws governing their structure.

The purpose of the present investigation was determination of the geometrical structure of the antimony sesquioxide molecule in vapor form by the electron-diffraction method. The MGU electron-diffraction apparatus was used for the work [4]. Commercial antimony sesquioxide of "pure" grade was used. The compound was evaporated from a molybdenum ampule at 300-400°. The s^2- and s^3-, one- and two-leaf sectors were used in taking the electron-diffraction patterns. A total of 12 series of electron-diffraction patterns (3 photographs in each series) was obtained from antimony sesquioxide vapor at electron wavelengths of 0.0371-0.0569 A; several series were measured visually and the rest were analyzed photometrically. Two methods were used for interpretation of the patterns – the variant of J. Karle and I. L. Karle of the radial distribution method, and the method of successive approximations [5-8] with the aid of photometric data.

The D(r) radial distribution curve based on experimental data is shown in Fig. 1. For the calculation, the initial region of the $I_{expt.}(s)$ intensity curve, which cannot be determined experimentally, was found by extrapolation of the theoretical $I_{theor.}(s)$ curve for a preliminary model found by visual treatment of the diffraction patterns. The D(r) curve has three distinct peaks, at 2.00, 2.90, and 3.61 A; the last has appreciable asymmetry ("shading off" on the right-hand side), indicating the overlapping of several peaks corresponding to interatomic distances close to each other in magnitude. The resultant radial distribution curve is satisfactorily interpreted with the assumption of a dimeric Sb_4O_6 molecule (T_d symmetry) with configuration analogous to that found earlier for P_4O_6 and As_4O_6 [1,2,3]. In this model (Fig. 2), four antimony atoms are at the vertices of a regular tetrahedron, each being linked to three oxygen atoms lying on the perpendiculars drawn through the centers of the tetrahedron edges. The first peak then represents $Sb_{(1)} - O_{(5)}$ interatomic distance, the second the distance between the $O_{(6)} \ldots O_{(10)}$ atoms, and the third may represent a combination of three interatomic distances: $Sb_{(1)} \ldots Sb_{(2)}$, $Sb_{(1)} \ldots O_{(8)}$ and $O_{(9)} \ldots O_{(10)}$. This assignment of the peaks on the D(r) curve gives the following values for

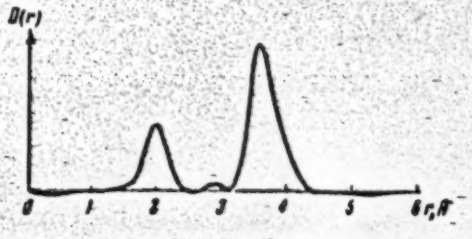


Fig. 1. D(r) radial distribution curve for the Sb_4O_6 molecule.

*In [3] only the parameters of the As_4O_6 molecule are given, but detailed experimental data are lacking.

two parameters of the Sb_4O_6 molecule: r(Sb – O) = 2.00 Å and < SbOSb = 129°. It should be noted that one of the possible models of the Sb_2O_3 monomer molecule (with configurations considered in a study of the structure of the B_2O_3 molecule [9]) is not in agreement with this radial distribution curve.

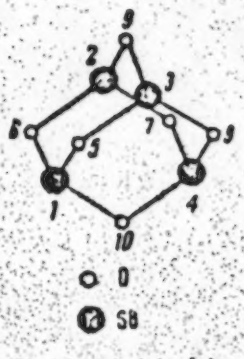
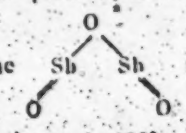


Fig. 2. Model of the Sb_4O_6 molecule.

We now turn to the method of successive approximations. Figure 3 shows the theoretical intensity curves of the two most probable models of the Sb_2O_3 monomer molecule: 1) the bipyramid type (three oxygen atoms form a regular triangle with one antimony atom on each side of the plane of the triangle at equal distances from it); 2) the plane angular model of the  type with the angle SbOSb = = 95°; and 3) the same as 2, but with the angle 129°.

Comparison of these curves with the experimental curve in the same diagram shows that curves 1 and 2 do not agree with the experimental curve, while curve 3, although it reproduces some individual characteristics of the experimental curve, has ratios of the heights of the third and fourth, and of the fifth and sixth maxima which differ from the experimental. On these grounds, monomeric Sb_2O_3 models should be rejected. On the other hand, the theoretical intensity curve 4 for the Sb_4O_6 model with T_d symmetry (Fig. 2) with r(Sb – O) = 2.00 Å and ∠ SbOSb = 129° is in good agreement with the experimental (calculation of these curves was based on effective root-mean-square vibration amplitudes of pairs of atoms, found from the D(r) curves in accordance with [5]). Thus, the data obtained by the method of successive approximations are in agreement with the results of analysis of the radial distribution curve.

TABLE. Comparison of the Geometrical Parameters of the P_4O_6, As_4O_6, and Sb_4O_6 Molecules

Molecule	E – O interatomic distance, Å	Angle EOE	Angle OEO	Literature
P_4O_6 in vapor	1.67 ± 0.03	128.5 ± 1.5°	98.5°	[1]
P_4O_6 in vapor	1.65 ± 0.02	127.5 ± 1°	99°	[2]
As_4O_6 in vapor	1.80 ± 0.02	126.0 ± 3°	100°	[2]
As_4O_6 in vapor	1.78 ± 0.02	128.0 ± 2°	99°	[3]
As_4O_6 in crystal	1.80	131°	98°	[10]
Sb_4O_6 in vapor	2.00 ± 0.02	129.0 ± 2.5°	98°	This paper
Sb_4O_6 in crystal	2.0	130°	96°	[10]

The following parameters were found for the Sb_4O_6 molecule with T_d symmetry (Fig. 2): r(Sb – O) = 2.00 ± ± 0.02 Å, ∠ SbOSb = 129 ± 2.5°.

It is interesting to compare (see table) the values found for the parameters of the Sb_4O_6 molecule with those of the previously studied P_4O_6 and As_4O_6 molecules both in the vapor phase and in the crystalline state because, according to x-ray diffraction data [10], crystals of the cubic modifications of antimony and arsenic sesquioxides consist of individual dimeric E_4O_6 molecules (there are no data on P_4O_6 molecules in crystals). The first striking point is that the parameters of the Sb_4O_6 molecule, like those of the As_4O_6 molecule, in the gas phase and in the crystalline state, virtually coincide. This agreement is apparently the consequence of the weak influence of intermolecular forces in crystals of these compounds on the configuration and geometrical parameters of the molecules forming them. Further, it is interesting to note that in E_4O_6 molecules the valence angle of the oxygen atom remains satisfactorily constant at 126-131°. The same applies to the valence angles of the P, As, and Sb atoms, which have the value of 97-100°. It follows that the geometrical configuration of molecules of the E_4O_6 type (E = P, As, Sb) does not alter when one E atom is replaced by another. Thus, the sesquioxides of phosphorus, arsenic, and antimony exhibit a close similarity, manifested in the formation of crystal lattices of the molecular type in which individual E_4O_6 molecules may be detected, and in the presence of dimeric molecules in the vapors; in the agreement between the geometrical parameters of E_4O_6 molecules in the gas phase and in the crystalline phase; and in the constancy of the O, P, As, and Sb valence angles.

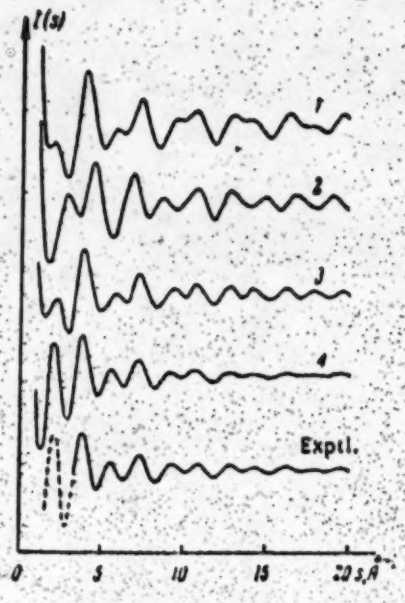


Fig. 3. Theoretical intensity curves for various models of Sb_2O_3 and Sb_4O_6 molecules, and the experimental curve.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF MOLECULES WITH CONJUGATED DOUBLE BONDS

1. α-CHLOROACROLEIN AND METHYLGLYOXAL

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 545-550, September-October, 1961
Original article submitted October 9, 1960

The molecular structure of α-chloroacrolein and methylglyoxal has been studied for the first time, by the electron-diffraction method with visual estimations of intensity. The principal parameters of the O = CH − ClC = CH_2 molecule are: r(C − H) = 1.08 A (assumed; r(C − Cl) = 1.72 ± 0.01 A; r(C = O) = 1.22 ± 0.03 A; r(C = C) = 1.31 ± 0.03 A; r(C − C) = 1.51 ± ± 0.03 A; ∠C = C − Cl = 126 ± 1.5°; ∠C = C − C = 119 ± 2°, and ∠O = C − C = 116 ± 2°; the rotation angle of C = O and C = C bonds from the trans configuration is α = 57 ± 5° for one rotational isomer and from the cis configuration for the other rotational isomer it is α = 41 ± 5° with the isomers in 2:1 ratio. For the planar O = CH − CH_2C = O molecule the values are: r(C − H) = 1.09 A (assumed); r(C = O) = 1.19 ± 0.02 A; r(C − C) = 1.47 ± 0.03 A; r(C − CH_2) = = 1.55 ± 0.03 A; ∠O = C − C = 126 ± 3°, and ∠O = C − CH_2 = 120 ± 3°. The possibility of nonplanar structure in molecules with conjugated double bonds is demonstrated. The relationship between the length of the C − C bond between two conjugated groups and the mutual rotation angle of these groups is discussed.

Study of the rotational isomerism of molecules with conjugated multiple bond systems is of great interest in relation to the theory of organic structure; various physical and physicochemical methods are used for this purpose. Among them a special place belongs to direct structural methods. These were the methods whereby it was demonstrated that molecules of aromatic compounds (derivatives of diphenyl and nitrobenzene) may have nonplanar structure; it was found that the rotation angles of the planes of conjugated rings and groups about single C − C and C − N bonds vary from 0 to 90°, in accordance with the magnitude of the steric hindrance [1-4]; However, the literature contains very few reliable structure data on the role of steric hindrance in the simplest molecules with conjugated double bonds. In our attempt to determine the configuration of the chloroprene molecule [5] we were unable to decide conclusively whether the structure of this molecule is planar or nonplanar. We therefore undertook an investigation of the structure of α-chloroacrolein and methylglyoxal molecules, whereby their configuration could be determined more conclusively.

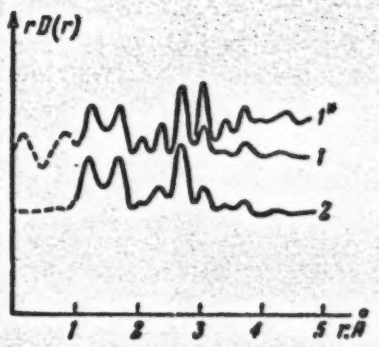


Fig. 1.

α-Chloroacrolein was synthesized as described in [6]; b.p. 29-31° (17 mm). Methylglyoxal was synthesized as described in [7]; b.p. 50-52° (15 mm). The electron-diffraction patterns of the vapors of the substances under investigation were obtained with the apparatus described earlier [8]. The diffraction patterns were interpreted on the basis of visual assessments of intensity, by two methods – radial distribution and successive approximations [9] – with the aid of the equations:

$$rD(r) = \Sigma sI(s) \exp(-as^2) \sin sr\Delta s, \quad (1)$$

where $s = \frac{4\pi}{\lambda} \sin \vartheta/2$, λ is the wavelength; ϑ is the scattering angle; I(s) is the scattering intensity; $\exp(-as^2_{max}) = 0.1$; and $\Delta s = 0.2$ A^{-1}, and

$$I(s) = \sum_{i \neq j} n Z_i Z_j \exp(-b_{ij} s^2) \frac{\sin sr_{ij}}{sr_{ij}}, \qquad (2)$$

where $Z_{i(j)}$ are the nuclear charges of the i(j) atoms, $b_{ij} = l^2_{ij}/2$, and l_{ij} is the root mean square amplitude of the thermal vibrations. The following values were assumed in the calculations: b = 0.0022 for C – H, 0.0043 for O...H and C...H, and 0 for all other pairs of atoms.

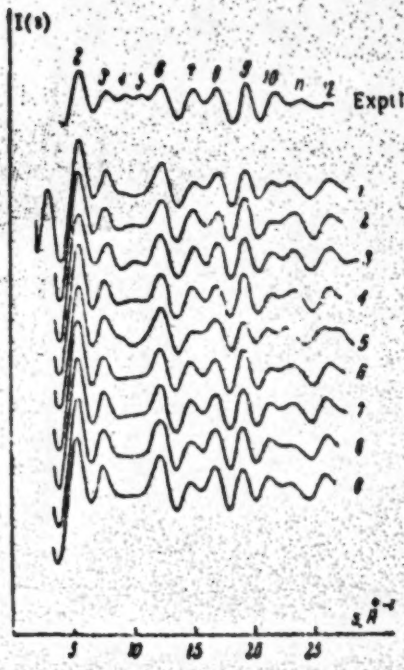


Fig. 2.

α-Chloroacrolein. Seven series of electron-diffraction patterns (with four plates in each series) were obtained for α-chloroacrolein vapor at $\lambda \approx 0.055$ A.

An experimental intensity curve (Table 1, Fig. 2) was plotted from the values of s and I(s) measured at the maxima and minima. Several rD(r) radial distribution curves were calculated. The following rD(r) curves are given in Fig. 1: 1) the experimental curve obtained with extrapolation of I(s) in the region s = 0-3.5 A^{-1} from the best theoretical curve, 8 (Fig. 2); 2) the theoretical curve, which is the Fourier transform of the theoretical intensity curve 8. Above the radial distribution curve 1 there is the segment 1* of an rD(r) curve calculated without zero extrapolation of I(s) and without an artificial temperature factor in Eq. (1). This curve shows that extrapolation of $I(s)_{expt.}$ to zero has little effect on the relationship between peaks 6, 7, and 8. The peaks of curve 1 are assigned to the following interatomic distances (in A) in the molecules of cis and trans α-chloroacrolein:

1) 1.26 – r(C – H), r(C = O), r(C – C'), r(C = C); 2) 1.72 – r(C – Cl); 3) 2.08 – r(C...H), r(O...H); 4) 2.38 – r(C'...O), r(C...C''); 5) 2.72 – r(C...Cl), r(C''...Cl); 6) 3.06 – r(O...Cl) for the trans form, r(C...O) for the cis form; 7) 3.38 – r(C''...O) for the trans form, and 8) 3.72 – r(O...Cl) for the cis form. The first peak could not be resolved in calculation of the rD(r) curve with a = 0; attempts to subtract the main peaks 2 and 5 proved unsuccessful; resolution of peak 1 into two, 1.18 A [r(C – H) and r(C = O)] and 1.42 A [r(C = C) and r(C – C)] was achieved artificially by additional multiplication of I(s) by s. Considerable diffraction effects then appeared in the region of r = 0-1 A. However, the remaining structural peaks did not change in position to an accuracy of ±0.01 A.

The nonplanar α-chloroacrolein molecule is defined by nine principal parameters: r(C – H), r(C = C), r(C – C), r(C – Cl), ∠C = C – Cl, ∠C = C – C, ∠O = C – C and the rotation angle α of the C = O group relative to the vinyl group. Moreover, if there are two isomers, two more parameters are added: the angle of deviation from the plane in the other isomer, and the relative contents of the rotational isomers. Analysis of the rD(r) curves shows that the molecules of both isomers are nonplanar, but it is possible to reduce the number of principal parameters to three by assuming r(C – H) = 1.08 A, r(C = O) = 1.22 ± 0.02 A and a value of 2:1 for the approximate ratio of the trans-to-cis forms (from the areas of the peaks). If r(C = C), r(C – C) and ∠C = C – Cl are taken as independent parameters, then the other parameters can be found from the rD(r) curves. In fact, a given value of the angle ∠C = C – Cl and r(C = C) determine r(C''...Cl). By using the mean value of r(C...Cl, C''...Cl), we can, from the rD(r) curve, find ∠C = C – C and then ∠O = C – C. The angle α is found from the principal parameters and r(O...Cl) for the trans form and r(O...Cl) for the cis form. The angles ∠O = C – H and ∠C = C – H were assumed to be close to 120°. The values of the independent parameters were refined by selection of experimental curves, and were

varied over the following ranges: ∠C = C − Cl from 120 to 126° in 3° steps, r(C = C) from 1.30 to 1.38 A, and r(C − C) from 1.46 to 1.54 A in 0.02 A steps (Fig. 2, Table 2). The best agreement was obtained for curve 8 (Table 1).

TABLE 1. Measurements of Electron-Diffraction Patterns

f (s)		α-Chloroacrolein		Methylglyoxal	
Max.	Min.	$s_{expt.}$	$s_{theor.}/s_{expt.}$ for model 8	$s_{expt.}$	$s_{theor.}/s_{expt.}$ for model 4
1				2,52	—
	1	4,03	(0,921)	4,38	0,968
2		5,05	(1,036)	5,65	1,037
	2	6,30	1,017	7,31	1,006
3		7,30	1,011	8,46	(0,940)
	3	8,45	—	10,18	1,002
4		8,96	—	11,19	1,014
	4	—	—	12,44	0,997
5		10,42	—	13,40	0,994
	5	11,96	—	15,45	0,968
6		12,92	1,003	16,67	0,980
	6	13,38	1,001	—	—
7		14,58	1,005	18,07	0,968
	7	15,63	0,996	20,36	0,968
8		16,64	1,001	21,66	1,016
	8	17,87	1,000	—	—
9		19,01	1,000	—	—
	9	20,22	0,995	—	—
10		21,34	0,996	—	—
	10	22,58	0,983	—	—
11		23,60	0,980	—	—
	11	24,98	0,986	—	—
12		26,13	0,996	—	—
Mean			0,998 ± ±0,006		0,994 ± ±0,018

TABLE 2. Parameters of the Theoretical Curves

	α-Chloroacrolein*			Methylglyoxal**			
	C = C, A	C − C, A	∠C=CCl,°	C − C', A	C' − C'', A	∠OCC',°	∠O'C'C'',°
1	1,36	1,48	123	1,48	1,56	123	123
2***	1,34	1,50	123	1,48	1,58	123	123
3****	1,34	1,50	123	1,46	1,58	127	120
4	1,34	1,52	123	1,48	1,56	126	120
5	1,30	1,54	123	1,52	1,52	123	120
6	2,36	1,48	126	1,48	1,56	126	123
7	1,34	1,50	126	1,52	1,52	123	123
8	1,32	1,52	126	1,48	1,56	126	126
9	1,30	1,54	126	1,52	1,52	123	126

*The following parameters (in A) were not varied: r(C = O) = 1.22; r(Cl...O) = 3.07; r(C − Cl) = 1.72; $r(Cl...O)_{cis}$ = 3.72; r(C − H) = 1.08; $r(C...O)_{trans}$ = 3.41; r(C...H) = = 2.08.

**The following parameters (in A) were not varied: r(C = O) = 1.20; r(C − H) = 1.09; r(O...O') = 3.48; r(C'...H'') = 2.16.

***For 1:1 mixture of trans:cis isomers.

****For the trans form of α-chloroacrolein only.

The divergence in the region of maxima 3 and 4 may be attributed to errors in visual determinations of intensity. The rD(r) curve plotted for model 8 agrees with the experimental radial distribution curve 1 (see Fig. 1). Another

molecular model, with the parameters: r(C = C) = 1.30 A, r(C – C) = 1.50 A and ∠CCCl = 126°, virtually coincides with model 8. The following average values were adopted as the final parameters: r(C – H) = 1.08 A (assumed), r(C–ECl) = 1.72 ± 0.01 A; r(C = O) = 1.22 ± 0.02 A; r(C = C) = 1.31 ± 0.03 A; r(C – C) = 1.51 ± 0.03 A; ∠C = = C – Cl = 126 ± 1.5°; ∠C = C – C = 119 ± 2°, and ∠O = C – C = 116 ± 2°, ∠α (from the trans configuration) = = 57 ± 5° and ∠α (from the cis configuration) = 41 ± 5° with a trans:cis ratio of 2:1.

Methylglyoxal. Seven series of electron-diffraction patterns were obtained for methylglyoxal vapor.

The experimental intensity curve was plotted from the values of s and I(s) measured at the maxima and minima (Table 1, Fig. 4). The rD(r) curve was calculated with zero extrapolation of $I(s)_{expt}$ from the theoretical curve for the planar model based on data for glyoxal and dimethylglyoxal [10]. The peaks of the rD(r) curve are assigned to the following interatomic distances (in A) in the planar molecule:

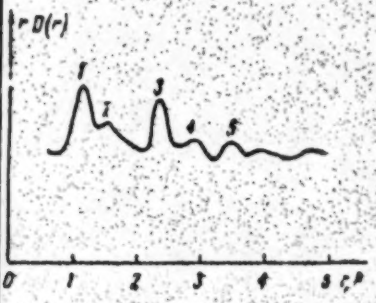


Fig. 3.

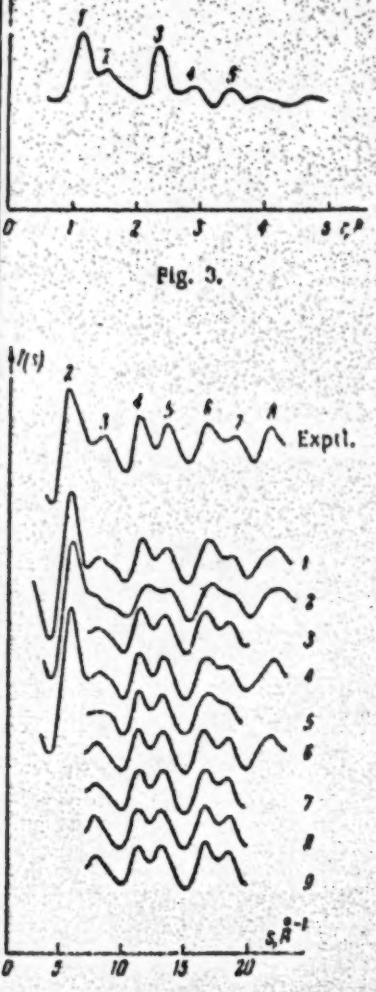
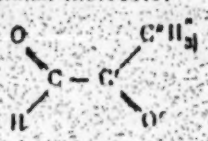


Fig. 4.



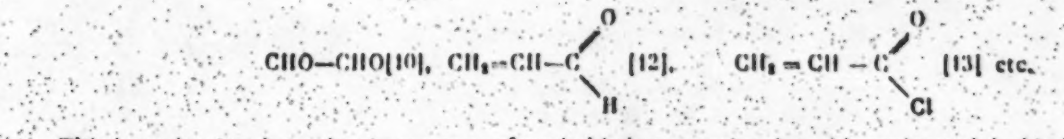
with C_s symmetry and with the H and H'' atoms in the cis position relative to the O' atom: 1) 1.17$_5$ – r(C – H), r(C = O); 2) 1.50 – r(C – C'), r(C' – C''); 3) 2.39 – r(C'...O), r(C...O'), r(C''...O'), r(C...C''), r(C'...H''), r(O...H); 4) 2.89 (diffuse) – r(O...C''), r(C...H''), r(O...H''), r(O'...H''); 5) 3.48 – r(O...O'), r(C''...H), r(C...H'').

The more distant peaks are of no significance and are comparable to diffraction effects. The conclusion that the methylglyoxal molecule is planar follows from a comparison of the rD(r) curves for the glyoxal [10] and methylglyoxal molecules, as the 3.48 A peak on the rD(r) curve for methylglyoxal, due mainly to the O...O'-trans distance, agrees within the limits of experimental error with the value of 3.45 A for the corresponding distance in the planar glyoxal molecule. This distance in dimethylglyoxal, determined with less precision [10], is 3.50 A. In general, the difference between the O...O' distances in the methylglyoxal and glyoxal molecules may be attributed to a difference between the OCC valence angles.

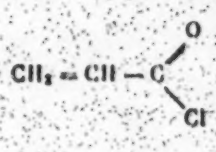
After the general configuration of the molecule had been determined, its principal parameters were refined. The rD(r) curve calculated without a temperature factor gave good resolution of the first two peaks, at 1.18 and 1.52 A. From the former we have r(C = O) = 1.20 ± 0.02 A. Refinement of r(C – C') and r(C' – C'') distances and of OCC' and OC'C'' angles was effected by selection of theoretical curves. The angles OCC' and CC'O' were assumed equal so as to reduce the number of parameters. The parameters were varied for two average values of r_{av}(C – C', C' – – C'') = 1.52 and 1.50 A, and three values of ∠O'C'C'' = 120, 123, and 126° (Table 2); some of the I(s) curves are given in Fig. 4. Curve 4 gives the best agreement with the experimental curve. The assumed equality of the OCC' and O'C'C angles is justified within the limits of experimental error (about ± 3°). Thus, for the values r(C = O) = 1.20 A, r(C – C') = = 1.48 A, and r(O...O') = 3.48 A the following values are found for the OCC' and O'C'C angles: 1) with ∠OCC' = = 123°, ∠O'C'C = 129.5°, and 2) with ∠OCC' = 120°, ∠O'C'C = 135.3°. However, a difference of about 15° between the OCC angles is improbable. The theoretical curve calculated for a molecular model with the parameters r(C = O) = 1.24 A, r(C – CH_3) = 1.52 A, r(C – C') = 1.48 A; ∠OCC' = 123°, ∠CC'O' = O'C'C'' = 118.5° (in accordance with data for acetone [11]) does not agree with the experimental curve. The following values were accepted as the final parameters for the planar configuration of the methylglyoxal molecule: 1) r(C – H) = 1.09 A (assumed); 2) r(C = O) = 1.19 ± 0.02 A; 3) r(C – C) = 1.47 ± 0.03 A; 4) r(C – CH_3) = 1.55 ± 0.03 A; 5) ∠OCC = = 126 ± 3°, and 6) ∠OC – CH_3 = 120 ± 3°.

DISCUSSION

The geometrical structure of the α-chloroacrolein and methylglyoxal molecules was studied for the first time in this investigation. The main geometrical parameters (bond lengths and valence angles) of these molecules are consistent with data for similar molecules, such as



This investigation shows that in presence of steric hindrance molecules with conjugated double bonds may be substantially nonplanar, as in the case of α-chloroacrolein. The planar structure of dimethylglyoxal is probably attributable to forces of attraction between the oxygen atom and the methyl group, which has an intermolecular radius equal to that of the chlorine atom. The isomeric acrylyl chloride molecule



has planar trans configuration, which corresponds to lower steric repulsion between the chlorine atom and the CH_2 group. The possibility of nonplanar structure in simplest diene molecules was confirmed by us earlier in the case of the isoprene molecule $CH_2 = CH - CH_3C = CH_2$ [14], which has nonplanar trans form with an angle of about 50 ± 10° between the planes of the vinyl groups.

The relationship between the length r of the central bond between two double bonds or phenyl rings, and the angle α between the planes of the double bonds still remains obscure. This is due to the lack of sufficiently precise experimental data and to the absence of a theoretically established r = r(α) relationship. Thus, if we use an empirical relationship of the form r = a + bα [3], analysis of the experimental data gives 0.066 A for the maximum change of r when α is varied from 0 to 90°, with a root mean square error of 0.015 A. However, correlation of the most precise structural data for a number of molecules provides no evidence of such a relationship (within the limits of experimental error):

Compound	r(C – C) in A	α	Literature
Butadiene	1.48 ± 0.01	0°	[15]
Diphenyl	1.49 ± 0.01	41.6°	[16]
Cyclooctatetraene	1.462 ± 0.001	56.3°	[17]
Hexaphenylbenzene	1.52 ± 0.01	90.0°	[4]

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COORDINATION NUMBERS OF CERTAIN IONS IN AQUEOUS SOLUTIONS, AND EFFECT OF TEMPERATURE ON THEM

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 551-557, September-October, 1961
Original article submitted May 18, 1961

The changes Δn_i of the coordination numbers of K^+, NH_4^+, and Cl^- ions with temperature in dilute aqueous solutions have been determined. These values were used for finding values of Δn_i for alkali metal cations and the Br^- and I^- anions by a thermochemical method. In the cases studied, the observed values of Δn_i are determined primarily by the relative dimensions of the particles in solution (ions and water molecules).

In investigations of ion hydration in aqueous solutions much importance attaches to the average number of water molecules constituting the closest environment of the ion; this is known as the coordination number of the ion in solution.

Such numbers are now approximately known in a number of cases. For example, the coordination numbers of several univalent ions in dilute aqueous solutions are close to four [1,2]. This value was found with most certainty in the case of the K^+ ion from Brady and Krause's x-ray diffraction data on aqueous KOH solutions [3]. It had been concluded earlier that in such cases the structure of the solution conforms to the condition of the least possible change in the structure of water during formation of the solution [2]. Coordination numbers of ions are close to four when the interaction of the ions with the nearest water molecules is relatively weak. At the same time, the coordination numbers of ions in aqueous solutions are often close to six, as has been demonstrated quite clearly for the cations Co^{2+} [4], Cu^{2+} [5], and Er^{3+} [6]. It has been shown, in the case of Co^{2+} as an example, that at concentrations below 2 M in aqueous chloride solutions and below 2.5 M in aqueous nitrate solutions the nearest environment of the cation consists of water molecules only [4].

A very important characteristic of the coordination numbers of particles in liquids is that these numbers are associated with thermal, primarily translational, motion of the particles. The more "lively" the translational motion, the greater (in general) is the number of local rarefactions in the liquids, and accordingly the less is the coordination number. This also applies to the coordination numbers of ions in aqueous solutions (ionic fields have symmetry which is close to spherical). The coordination numbers of ions are influenced by the frequency of exchange of their nearest water molecules; the coordination number diminishes somewhat with increase of exchange frequency [2]. Obviously the influence of exchange on the coordination number is especially pronounced in the case of ions having relatively weak interaction with water (alkali-metal cations, halide anions). It is with these ions that the present investigation is concerned.

The effect of temperature on the coordination numbers of ions in aqueous solutions is of considerable interest. An experimental method for investigation of this relationship was described earlier [7]. Calculations of the changes of coordination numbers with temperature are based on experimental determinations of the heats of solution L of salts in aqueous HCl solutions of various concentrations m at different temperatures; the following formula is used:

$$\Delta\beta = k_T \beta + K\left(\frac{\Delta n_к}{h_к} - \frac{\Delta n_а}{h_а}\right), \qquad (1)$$

where $\beta = -\Delta L/\Delta m$ (or $\Delta L/\Delta m$ if the thermodynamic convention of signs is used; here ΔL denotes the change of L when the concentration is changed by Δm) is referred to some particular temperature, such as 25°; $\Delta\beta$ is the change of β when the temperature is raised by 10°; Δn_c and Δn_a are changes in the coordination numbers of the cation and

anion, respectively, when the temperature is raised by 10°; R_c and R_a are the radii of the first coordination spheres of the ions, assumed (as an approximation) to be independent of temperature; K and k_T are constants determined experimentally. Equation (1) can be used for finding changes in the coordination numbers of ions with temperature if the constants K and k_T and the value of Δn_i for any ion are known. In [7], Eq. (1) was used for finding Δn_i for alkali-metal cations and the Cl^- anion. A value of K found earlier [2] was used for this purpose. In the present investigation the constants K and k_T were found somewhat differently. The proposed method is based on the possibility of determining, independently of the thermochemical method, the changes of coordination numbers with temperature in dilute aqueous solutions for the K^+, NH_4^+ cations and the Cl^- anion.

TABLE 1. Heats of Solution of NH_4Cl, KBr, and KI in Aqueous HCl Solutions

Salt	t°, C	m	L	Salt	t°, C	m	L
NH_4Cl	15	0,00	−4,11	KBr	35	0,00	−4,54
		0,72	−4,21			0,77	−4,68
		1,44	−4,24			1,32	−4,64
		2,23	−4,28			1,57	−4,65
		2,88	−4,37			2,40	−4,66
	25	0,00	−3,80			3,09	−4,65
		0,72	−4,01	KI	15	0,00	−5,34
		1,44	−3,99			0,70	−5,27
		2,35	−4,15			1,42	−5,11
		2,88	−4,19			2,18	−4,94
	35	0,00	−3,51			2,99	−4,92
		0,82	−3,67		25	0,00	−5,01
		1,64	−3,84			0,72	−4,94
		2,35	−3,95			1,45	−4,89
		2,88	−3,99			2,24	−4,80
KBr	15	0,00	−5,33			3,06	−4,63
		0,85	−5,25		35	0,00	−4,58
		1,36	−5,18			0,95	−4,63
		2,06	−4,97			1,42	−4,53
		2,82	−4,84			1,94	−4,56
	25	0,00	−4,81			2,21	−4,55
		0,65	−4,94			3,07	−4,51
		1,31	−4,87				
		2,00	−4,89				
		2,73	−4,84				

Earlier [8] an approximate equation was derived, connecting the temperature variation Δn_i of the coordination number of an ion in solution with the coordination number n_i itself, and with ΔE_i, the change produced by the ion in the value of the potential barrier for translational motion of water molecules in solution as compared with the corresponding value for pure water:

$$\Delta n_i = \frac{n_i}{n}\left(\Delta n - 10n\frac{\Delta E_i}{RT^2}\right). \qquad (2)$$

The results of x-ray diffraction studies of water at 25° give n = 4.6 and Δn = 0.07. Equation (2) is valid near the boundary between positive and negative hydration. It is therefore applicable to the K^+ ion (the crystal radius of the K^+ ion is 1.33 A). At the same time, according to x-ray data [3], the coordination number of the K^+ ion in dilute aqueous solutions at 25° is about 4. Taking $n_{K^+} = 4$ and using the value found earlier [2] for ΔE_{K^+}, we can use Eq. (2) for approximate determination of Δn_{K^+}. It is found to be +0.12.*

The values of $\Delta n_{NH_4^+}$ and Δn_{Cl^-} can be determined independently of the thermochemical method because of the peculiar properties of aqueous ammonium chloride solutions. Fajans and Johnson [9], in their studies of the partial molar volumes of numerous electrolytes in aqueous solutions, found that the partial molar volume in dilute aqueous solution at 25-35° is almost exactly equal to 2V, double the molar volume of water, and that it varies in

*The value given earlier [7,8] was +0.10; this is because n_{K^+} was taken as 3.8.

the same way as 2V with temperature in this region. According to Fajans and Johnson, equal but opposite action of NH_4^+ and Cl^- ions on water is improbable, because ammonium chloride solutions and water are similar with regard not only to the partial molar volumes, but also to many other properties (molar partial entropy, viscosity, infrared absorption spectra, electron diffraction, etc.). Fajans and Johnson assume that the ionic volumes of NH_4^+ and Cl^- (at infinite dilution) are equal to the molar volume of water and that both quantities depend equally on temperature.

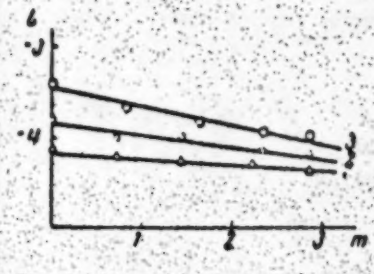

Fig. 1. Heats of solution of ammonium chloride in aqueous HCl solutions at various temperatures: 1) 15°; 2) 25°; 3) 35°.

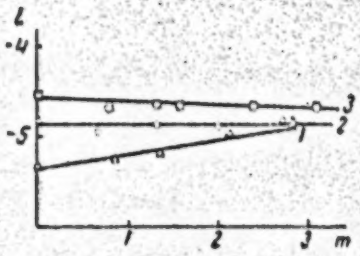

Fig. 2. Heats of solution of potassium bromide in aqueous HCl solutions at various temperatures: 1) 15°; 2) 25°; 3) 35°.

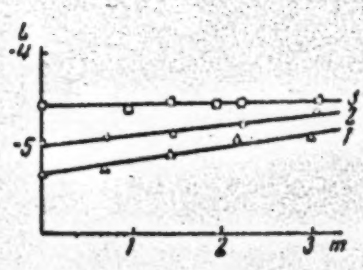

Fig. 3. Heats of solution of potassium iodide in aqueous HCl solutions at various temperatures: 1) 15°; 2) 25°; 3) 35°.

The molar volume of a liquid depends on many quantities; in particular, on the mean distances between the nearest particles (determined by the particle size and thermal motion, mainly vibrational), the mutual orientation of the particles (this is significant in the case of particles with symmetry appreciably different from spherical), and the average coordination number of the particles (associated with their translational motion). Undoubtedly the dependence of the liquid volume on the coordination number of the particles is the most significant. Incidentally, this follows from the fact that the average number of local rarefactions in the liquid is associated with the coordination number [2,10]. Since the molar volume of the liquid is strongly dependent on the coordination number of the particles, it may be concluded that in the 25-35° region variations of the coordination numbers of ammonium and chloride ions with temperature are close to the corresponding variations of the coordination number of water molecules in water. The basis for this conclusion is that the respective ionic volumes and the molar volume of water depend similarly on temperature; its validity is associated with the fact that the distances between the nearest particles in aqueous electrolyte solutions apparently alter very little with temperature [2]. Therefore, we may assume that

$$\Delta n_{NH_4^+} \approx \Delta n_{Cl^-} \approx \Delta n \approx 0{,}07,$$

which appears quite reasonable for the ammonium ion, the radius of which is close to the "radius" of the water molecule, and which has four protons capable of forming hydrogen bonds with water molecules.

If we have values of Δn_i for K^+, NH_4^+, and Cl^-, we can write Eq. (1) for KCl and NH_4Cl. If the corresponding values of β and $\Delta\beta$ have been determined experimentally, K and k_T can be found from these two equations. The values of β and $\Delta\beta$ for KCl were found earlier [7]. In the present investigation they were determined for NH_4Cl. In view of the interest which attaches in the present investigation to the effect of temperature on the coordination numbers of the Br^- and I^- anions, the values of β and $\Delta\beta$ for KBr and KI were also determined.

Salts recrystallized from c.p. and analytical-grade reagents were used for the calorimetric experiments. The final salt concentrations in solution were 0.04 and 0.02 mole of salt per 50 moles of water in the cases of KBr and KI, respectively, and 0.07 mole of salt per 50 moles of water in the case of NH_4Cl. The method used for determination of the heats of solution (L) did not differ from that described earlier.*

The results are given in Table 1. The heats of solution are expressed in kcal per mole of dissolved salt. The hydrochloric acid concentration m is expressed in moles of HCl per 50 moles of water. The thermochemical sign convention is used.

*In the case of KI, the solution was slightly yellowish after the calorimetric experiments. However, it was shown (by titration with $Na_2S_2O_3$) that oxidation of I^- is slight (< 0.08%) and may be neglected.

Variations of the heat of solution L with m are plotted in Figs. 1-3. Values of β were found from experimental data by the method of least squares. The values of β and $\Delta\beta = \frac{1}{2}(\beta_{25} - \beta_{15})$ are:

Salt	β_{15}	β_{25}	β_{35}	$\Delta\beta$
NH_4Cl	81	128	201	60
KBr	−176	0	23	100
KI	−151	−118	−25	63

Equations (1) for KCl and NH_4Cl become:

$$76 = k_T \cdot 11 + K\left(\frac{0.12}{2.71} - \frac{0.07}{3.19}\right)$$
$$60 = k_T \cdot 128 + K\left(\frac{0.07}{2.81} - \frac{0.07}{3.19}\right),$$

and hence $K = 3.2 \cdot 10^3$ and $k_T = 0.399$. Knowing these constants and Δn_{Cl^-}, we can obtain values of Δn_i for alkali-metal cations which are probably more correct than those given in [1]; with the experimental values of β and $\Delta\beta$ for KBr and KI we can also find Δn_{Br^-} and Δn_{I^-}. The following values were found for Δn_i (the crystal ionic radii r_i according to [11] are also given):

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
Δn_i	−0.05	0.09	0.12	0.17	0.24	0.07	0.04	0.03
r_i	0.68	0.98	1.33	1.49	1.65	1.81	1.96	2.20

In Fig. 4 the values found for Δn_i are plotted against r_i. The resultant relationship is not monotonic: either there are two separate curves, for cations and anions respectively, or (if it is assumed that all the values of Δn_i refer to a common curve) the curve has a maximum at $r_i > r_{H_2O}$. In any event, the derivative $\partial \Delta n_i / \partial r_i$ changes sign in the transition from Li^+ to I^-.

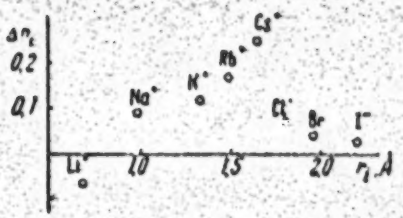

Fig. 4. Variations of Δn_i with r_i for alkali-metal cations and halide anions.

It seems that the most significant feature of the observed situation is the difference between $\left(\frac{\partial n_i}{\partial T}\right)_p$ and $\left(\frac{\partial n}{\partial T}\right)_p$, for example, $\delta_i = \left(\frac{\partial n_i}{\partial T}\right)_p - \left(\frac{\partial n}{\partial T}\right)_p$. The change of the solution structure, leading to a change of the "free water" content with change of temperature [7], is associated with the magnitude of δ_i. Evidently the curve representing the $\delta_i(r_i)$ relationship is of the same type as for the $\Delta n_i(r_i)$ relationship, but is displaced along the ordinate axis.* It is significant that for r_i in the $r_{Li^+} - r_{Cs^+}$ region the derivative $\partial \delta_i / \partial r_i > 0$, whereas in the $r_{Cl^-} - r_{I^-}$ region we have $\partial \delta_i / \partial r_i < 0$.

It was of interest to compare the results of the present investigation with calculations of the changes of coordination numbers with temperature for a liquid-solution model [12]. Suppose that we have a large number of spheres of radius r_a constituting the liquid, and suppose that a small number of spheres of radius r_b is added to this system of spheres. The spheres a are particles of solvent, and spheres b are solute particles. It is possible to calculate the dependence of $\left(\frac{\partial n_{ba}}{\partial T}\right)_p$ on the ratio of the radii $r_b / r_a = \epsilon$ (n_{ba} is the coordination number of spheres b in solution, i.e., the average number of spheres a surrounding each sphere b) and hence to find the $\delta_b(\epsilon)$ relationship.

We do not consider that this model is close to the types of aqueous electrolyte solutions studied here. Moreover, in the case of a model liquid solution consisting of spheres of two kinds (without interaction), the derivatives of the coordination number with respect to temperature must always be negative. It is likely, however, that investigation of such a model may be useful for elucidation of the nature of $\Delta n_i(r_i)$ relationships, and in particular for

*Dilute solutions are considered here, so that the values of $\left(\frac{\partial n_i}{\partial T}\right)_p$ for different ions may be regarded as independent.

finding the extent to which this relationship is determined by the specific interaction between ions and water molecules and by the relative dimensions of the particles in solution.

In Fig. 5, $\delta_b = \left(\frac{\partial n_{ba}}{\partial T}\right)_p - \left(\frac{\partial n_{aa}}{\partial T}\right)_p$ is plotted against ϵ. Figure 5 shows that the $\delta_b(\epsilon)$ relationship for this model is represented by a curve with a maximum at $\epsilon > 1$. The case of $\epsilon = 1$ corresponds to $r_b = r_a$.

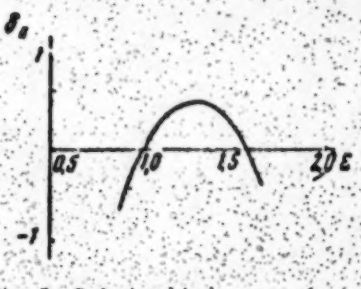

Fig. 5. Relationship between δ_i and ϵ for a liquid-solution model.

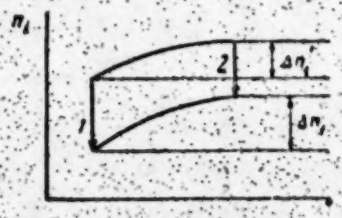

Fig. 6. Schematic explanation of the increase of the observed values of Δn_i.

Thus, the results of model calculations show that if the observed relationship between Δn_i and r_i is associated primarily with the relative dimensions of the particles rather than interaction characteristics, then this relationship is represented by a curve with a maximum at $r_i > r_{H_2O}$. The agreement between the calculated values of δ_b for the liquid-solution model and the experimental results of the present investigation appears to indicate relatively weak interaction (in the sense of energy changes at small distances from the particles [2, 13]) between the ions in question and water in solution. The existence of a common curve for cations and anions is by no means an essential condition for this. By agreement between the calculated values of δ_i for the model and the results of the present investigation we mean primarily the correspondence of the signs of the derivatives $\partial\delta_i/\partial r_i$ in the regions of small and large r_i.

The connection between these experimental results and the boundary between positive and negative hydration requires special consideration. It was shown in [7] that when $\Delta E_{i_0} = 0$, the value of Δn_i^0 should be 0.05. The value of Δn_i turns out to be smaller than the value of Δn_{Na^+} found in the present investigation. At the same time, it is known that the boundary between positive and negative hydration corresponds to the ionic radius $r_i^0 \approx 1.2$ A. This is possibly a consequence of lack of precision in the results, but if this discrepancy is not due to experimental error then it should probably be attributed to disturbance of the water structure by the ions.

It is well known [2, 14] that ions disturb the structure of water; this disturbance is most pronounced in the immediate vicinity of the ion and diminishes relatively rapidly with distance. This disturbance in itself leads to the existence of an energy contribution, which results in intensification of the translational motion of the water molecules nearest to the ion, and hence to a decrease of its coordination number. It is obvious that the corresponding contribution to the decrease of the coordination number diminishes with rise of temperature, since rise of temperature leads to breakdown of the water structure, so that the influence of the ions becomes weaker. It is easy to see that if the coordination number increases with temperature this situation leads to an increase of the observed values of Δn_i. In the schematic diagram in Fig. 6, the arrows 1 and 2 represent the contributions to the decrease of the coordination number due to disturbance of the water structure by the ion; Δn_i is the observed change of the coordination number of the ion with temperature, and $\Delta n'_i$ is the change which would occur without the contribution corresponding to breakdown of the structure. It may be seen that $\Delta n_i > \Delta n'_i$. This may account for the increase of the observed value of Δn_{Na^+} above the value which determines the boundary between positive and negative hydration.

The new numerical value of the constant K found in this investigation makes it necessary to modify somewhat the values given earlier for the coordination numbers of ions in dilute aqueous solutions at 25°. Using the values found earlier for β_{25} [2, 7] and the values of β_{25} for NH_4Cl, KBr, and KI found in the present investigation, we have the following values for the coordination numbers (the values of $\rho_i = n_i/4\pi R_i^2$, the surface distribution densities of water molecules in the first coordination layer at 25° are also given; it will be remembered that for water at 25°, $\rho^* \cdot 100 = 4.4$).

Ion	Li^+	Na^+	K^+	NH_4^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
n_i	3.4	3.6	4.0	4.3	4.2	4.2	4.7	4.9	5.2
$\rho'_i \cdot 100$	6.4	5.1	4.3	4.3	4.0	3.6	3.7	3.5	3.2

In conclusion, we thank Yu. M. Kessler for very useful discussions and valuable advice.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

INVESTIGATION OF ANTIOXIDANT RADICALS BY THE ELECTRON PARAMAGNETIC RESONANCE METHOD

1. PHENOXY RADICALS

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 558-561, September-October, 1961
Original article submitted July 14, 1960

The EPR method was used for studying the structure of phenoxy radicals formed by the interaction of benzoyl peroxide and cyclohexyl percarbonate with certain substituted phenols. It is shown that the unpaired electron is delocalized along the system of π bonds of the benzene ring, its highest density being concentrated in the para position to the oxygen atom. The phenoxy radicals of 2,6-di-tert-butyl-4-methylphenol, 2,4,6-tri-tert-butylphenol, p-aminophenol, α-naphthol, and other phenols were studied. It is shown that the life of phenoxy radicals is measured in hours.

It is known that alkyl-substituted phenols are effective oxidation inhibitors [1]. In the opinion of a number of workers [2], the mechanism of their inhibiting action consists of termination of the kinetic oxidation chains and replacement of the $RO_2^{\cdot}$ peroxide radicals leading the oxidation chains by stable phenoxy radicals, incapable of continuing the chains, by the reaction

$$RO_2^{\cdot} + PhOH \rightarrow RO_2H + PhO^{\cdot}. \qquad (1)$$

The effectiveness of phenols as inhibitors is determined by the rate of this reaction, which depends on the stability of the O – H bond in the phenol.

According to the concepts developed by N. N. Semenov [3], the energy of an X – Y bond may be represented as follows:

$$Q_{XY} = E_{XY} - B_{X\cdot} - B_{Y\cdot}, \qquad (2)$$

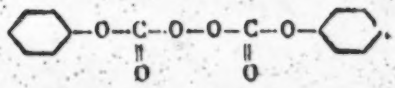
where Q_{XY} is the experimental value of the bond energy; E_{XY} is the energy required to break the bond on the assumption that the electron configurations of the X and Y radicals are unchanged; $B_{X\cdot}$ and $B_{Y\cdot}$ are the conjugation energies of X and Y.

Comparison of the rate constants of reaction (1) for various phenols with the vibration frequencies of the O – H bonds in the same phenols [4] shows that there is no distinct connection between the two. The O – H vibration frequency varies little with change of the substituent in the benzene ring, whereas the effectiveness of phenols as inhibitors is determined entirely by the nature of the substituent. Since the vibration frequency characterizes the magnitude of E_{OH} in Eq. (2), and this is determined by conjugation of the molecule, it is evident that introduction of a substituent has little influence on the conjugation of the molecule and on E_{OH}, and at the same time greatly influences the bond strength Q_{XY}. The probable cause of this relationship is the high conjugation energy of phenoxy radicals $B_{PhO\cdot}$ and its strong dependence on the nature of the substituents in the benzene ring. Because of the high conjugation energy, such radicals should be stable, and attempts may be made to detect and identify them.

Our investigation consisted of such an attempt to detect stable phenoxy radicals by means of electron paramagnetic resonance (EPR).

EXPERIMENTAL

Phenols of various structures were used for the investigation. The sources of active radicals capable of detaching hydroxyl hydrogen from phenols to give phenoxy radicals were the unstable compounds, benzoyl peroxide,

cyclohexyl percarbonate  , and in some instances p-tert-butylcumene hydroperoxide, which decomposes with formation of oxy- and peroxy radicals in presence of catalysts.

All the experiments were performed in thin glass ampoules in toluene solution with the reacting components in 1:1 ratio. The reaction mixture was put in the ampoule, which was heated to 50-80° and then placed in the resonator of the EPR spectrometer [5]; the first derivatives of the absorption spectra were recorded by means of the EPP-09 recording potentiometer.

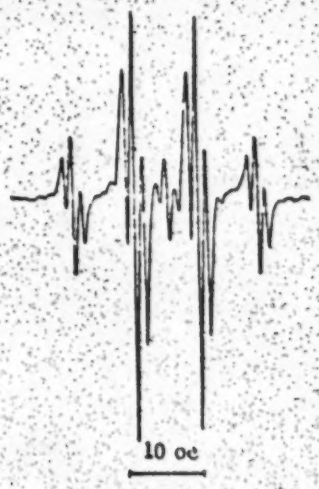


Fig. 1. EPR spectrum of the 2,6-di-tert-butyl-4-methylphenoxy radical.

RESULTS AND DISCUSSION

The EPR spectrum of the 2,6-di-tert-butyl-4-methylphenoxy radical is given in Fig. 1. The four main components with 1:3:3:1 intensity ratio probably arise by the interaction of the magnetic moment of the unpaired electron with the magnetic moments of the three protons of the methyl group situated in the para position to the oxygen atom. Splitting between the components amounts to 11 oersteds. Comparison of this value with the splitting between the components for the free methyl radical (about 25 oersteds) shows that the electron is strongly conjugated with the benzene ring. Indeed, each component of the quadruplet is split into three components with 1:2:1 intensity ratio (splitting 1.8 oersteds). This is evidently due to interaction of the electron with two protons in the meta position in the ring.

Such a spectrum is obtained after interaction of 2,6-di-tert-butyl-4-methylphenol with benzoyl peroxide and cyclohexyl percarbonate, and also on addition of diphenylpicrylhydrazyl (DPPH) to a solution of phenol in toluene. In the latter case the violet DPPH solution rapidly turns yellow at room temperature and the quadruplet of the phenoxy radical appears in the EPR spectrum instead of the DPPH quintuplet.

An exactly similar quadruplet is obtained on irradiation of 2,6-di-tert-butyl-4-methylphenol by fast electrons.*

Fig. 2. EPR spectrum of the 2,4,6-tri-tert-butylphenoxy radical.

Figure 1 shows that upon the basic spectrum described above there is superposed a much weaker signal of a radical of another and unknown type, which gives only a triplet in the center and weak peaks at the sides of the central components of the basic spectrum.**

The nature of the spectrum was not altered when a toluene solution of a mixture of benzoyl peroxide and 2,6-di-tert-4-methylphenol was heated at 100° for 2 hours with oxygen passed through the solution. The intensity of the signal merely diminished slightly.

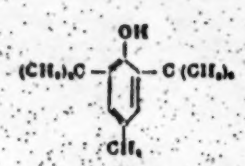
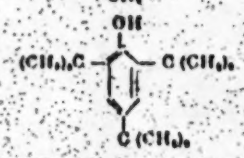
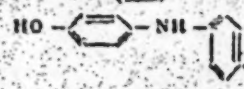
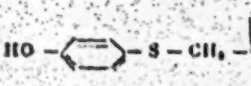
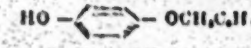
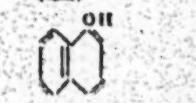
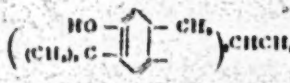
The spectrum of the 2,4,6-tri-tert-butylphenoxy radical is given in Fig. 2. The triplet probably appears owing to interaction of the electron with the meta protons of the benzene rings, and the splitting is 1.7-1.8 oersteds, as in the previous case.

EPR spectra in the form of a singlet, shown in Fig. 3a and 3b, are given by α-naphthol and p-aminophenol interacting with benzoyl peroxide and cyclohexyl percarbonate and by α-naphthol on catalytic decomposition of p-tert-butylcumene hydroperoxide in presence of cobalt stearate. The narrow singlet of the α-naphthyl radical (3 oersteds) may be attributed to strong conjugation of the unpaired electron with the π-bond system of the naphthyl ring.

*The experiment on irradiation by fast electrons was carried out jointly with A. T. Koritskii and A. F. Lukovnikov.

**The nature of the second radical has now been elucidated (see [8]).

Character of the EPR Spectra of Radicals of Substituted Phenols

Phenol	Form of spectrum	Splitting or line width (oersteds)
	quadruplet of triplets	11
	triplet	1,7—1,8
	singlet	11
	singlet	4,5
	singlet	5,5
	singlet	4,5
	singlet	3
	septet	1,7—1,8

Similar spectra were obtained for the radicals of hydroquinone monobenzyl ether, propyl gallate, and other phenols.

Figure 3c shows the spectrum of the radical of a substituted diphenol; this consists of seven components with poor resolution, and its interpretation is difficult as yet.

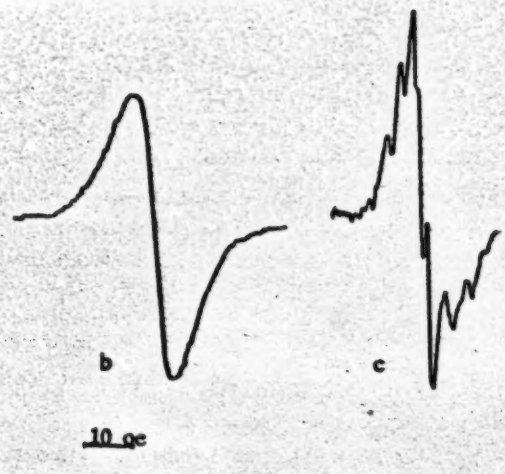
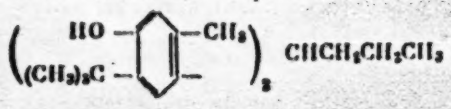


Fig. 3. EPR spectra of radicals formed from: a) α-naphthol; b) p-aminophenol; c) 

Spectra of radicals of hydroquinone, p-nitrophenol, p-cresol, and unsubstituted phenol (i.e., phenols without ortho substituents) could not be observed. It should be noted that most of such phenols are very weak antioxidants.

The formation of phenoxy radicals refutes the hypothesis that the reaction of benzoyl peroxide with phenols proceeds by a molecular mechanism [6].

The results of this investigation are confirmed by the data in a recent paper [7] (published during preparation of our paper for the press) reporting a study of stable phenoxy radicals formed by oxidation of phenols by lead dioxide. Our future investigations will be concerned with determinations of the kinetic characteristics of phenoxy radicals and studies of the structure of radicals obtained from other phenols.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

COMPARATIVE STUDY OF THE RAMAN SPECTRA OF ALLYL SILANES, GERMANES, AND STANNANES

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 562-568, September-October, 1961
Original article submitted November 18, 1960

The Raman spectra of allyl germanes and allyl stannane have been investigated. It is shown that the allyl group attached to Ge and Sn atoms (as in the case of Si) has a combination of characteristic frequencies, and the intensities of the corresponding lines increase additively with the number of allyl groups. When a quaternary C atom in a molecule is replaced by Si, Ge, or Sn, the general character of the change in the spectrum consists of a sharp intensity increase of the lines associated with vibrations involving the M atom, while the vibration frequencies decrease. The intensities and positions of the other lines alter little. It is shown that the specific interaction of the M atom with the C = C bond in the β-position relative to it is intensified when Si is replaced by Ge or Sn. The intensity of the line corresponding to vibration of the double bond increases roughly in geometrical progression.

Investigations of the mutual influence of atoms within molecules open up new possibilities for deepening our knowledge of the nature of the chemical bond. Our own investigations in this field are concerned with the changes produced in an organic molecule by replacement of a quaternary carbon atom by a hetero atom: silicon, germanium, or tin. This series is interesting because the character of the central atom alters from that of a typical nonmetal, carbon, through elements with intermediate properties (silicon and germanium), to a typical metal, tin.

Our earlier comparative studies of the chemical behavior and spectra of carbon and silicon compounds of similar structures [1-5] showed that the Si atom is capable of interacting with multiple bonds situated in the β-position to it, and that this effect in its spectroscopic and chemical aspects is analogous to conjugation of multiple bonds. In addition, the Si atom has the so-called "barrier" properties: the R substituents in the , molecule, where R represents alkyl, alkylene, or aryl radicals, have weak interaction with each other, and this leads to the appearance of characteristic frequencies for each of the R radicals attached to Si in the vibrational spectrum. We showed further [6-9] that these same properties are retained and even intensified in the spectrum of organogermanium and organotin compounds.

Up to now spectra of the following series of compounds have been studied from this standpoint: $(CH_3)_4M$ [10 to 14], $(CH_3)_3M-CH=CH_2$ [7], $(CH_3)_3M-CH_2-CH=CH_2$ [6,8]. The publications [10-14] report detailed investigations of the vibrational spectra of tetramethyl-substituted C, Si, Ge, and Sn (with calculations of the force constants and vibration frequencies); the intensities of the lines corresponding to fully symmetrical vibrations of the system have also been investigated [14]. From these investigations it may be concluded that the transition from C to Sn is accompanied by a decrease in the frequencies of the skeleton (with a decrease of the force constants between the M − C bonds) and an increase in the intensity of the Raman lines corresponding to vibrations in which the central M atom is involved to some extent. Raman spectra of vinyl derivatives of M (in the series from C to Sn) showed, in addition to the above-mentioned effects, a gradual decrease in the intensity of the line corresponding to vibration of the C = C double bond. In contrast to this, the Raman spectra of allyl derivatives of M [8] exhibited an increase in the intensity of the corresponding line, approximately in the proportion of 1:2:4:8 in the series C → Si → Ge→Sn.

In the present investigation we carried out a detailed study of the Raman spectra of allyl derivatives of group IV elements of the periodic system. The Raman spectra of the following compounds, the synthesis of which was described earlier [15], were obtained:

I. $(CH_3)_3C - CH_2 - CH = CH_2$*
II. $(CH_3)_3Ge - CH_2 - CH = CH_2$
III. $(CH_3)_2Ge(CH_2 - CH = CH_2)_2$
IV. $CH_3Ge(CH_2 - CH = CH_2)_3$
V. $(CH_3)_3Sn - CH_2 - CH = CH_2$

Data on frequencies and line intensities in the Raman spectra of $(CH_3)_3Si - CH_2 - CH = CH_2$, $(CH_3)_2Si(CH_2 - CH = CH_2)_2$ and $CH_3Si(CH_2 - CH = CH_2)_3$ were taken for comparison from [5].

The spectra were obtained by means of the ISP-51 apparatus with a central camera. The frequency positions were measured by comparison with the spectrum of an iron arc with the IZA-2 comparator. The intensities at the line maxima were measured by means of photographic photometry (with the MF-2 and MF-4 microphotometers) as described in [16], and expressed on the cyclohexane scale (the intensity at the maximum of the 802 cm^{-1} cyclohexane line was taken as 250 units). The comparison standard was the spectrum of $(CH_3)_2SiCH_2 - CH = CH_2$, the line intensities of which on the cyclohexane scale were reliably established in [5]. The intensities were calculated for equal numbers of molecules in the scattering volume by means of the formula $I_M = I_0 d_0 M_s / d_s M_0$, where I_M is the intensity for an equal number of molecules in the scattering volume, I_0 is the intensity per unit volume; d_0 and d_s are the densities of cyclohexane and the substance; M_0 and M_s are the molecular weights of cyclohexane and the substance. Data on the degree of depolarization ρ of the most intense Raman lines were also obtained.** A cylinder of appropriately oriented Polaroid film was fitted for this purpose onto the vessel with the scattering substance. Since we did not observe a number of conditions necessary for precise determination of ρ (for example, that the exciting rays should be strictly parallel), our data on the degree of depolarization are semiquantitative in character.

Raman Spectra ($\Delta\nu$ in cm^{-1})

The first number in parentheses is the line maximum intensity on the cyclohexane scale, referred to unit volume; the second is the degree of depolarization. The coefficient k for conversion of the intensity to an equal number of molecules in the scattering volume is given for each substance:

$$k = \frac{d_0 M_s}{M_0 d_s}$$

I. $(CH_3)_3C - CH_2 - CH = CH_2$

182 (10), 233 (8), 318 (25), 340 (30), 377 (10), 460 (10), 619 (40), 755 (70), 878 (20), 892 (5), 911 (3), 929 (22), 953 (5), 991 (5), 1024 (10), 1098 (15), 1139 (20), 1191 (30), 1237 (35), 1288 (50), 1410 (25), 1440 (35), 1640 (90).

$$k = \frac{0{,}7787 \cdot 98}{84 \cdot 0{,}6827} = 1{,}33$$

II. $(CH_3)_3Ge - CH_2 - CH = CH_2$

183 (150, dp), 198 (150 dp), 263 (30; 0.87), 400 (40; 0.30), 526 (160; 0.20), 572 (300; 0.18), 600 (160; 1.0), 688 (25; 0.44), 759 (15), 806 (5), 890 (25), 930 (4, dp), 990 (4, dp), 1145 (260; 0.52), 1195 (10; 0.82), 1243 (25, 0.48), 1300 (70; 0.30), 1398 (25; 0.62), 1420 (15), 1630 (250; 0.26), 2909 (320; 0.22), 2935 (20), 2973 (125; 0.89), 2994 (75; 0.28), 3080 (25; 0.80).

$$k = \frac{0{,}7787 \cdot 150}{84 \cdot 0{,}9952} = 1{,}48$$

III. $(CH_3)_2Ge(CH_2 - CH = CH_2)_2$

184 (200), 194 (200), 254 (10), 272 (8), 374 (40; 0.45), 401 (60; 0.37), 521 (140; 0.25), 537 (80; 0.73), 585 (145; 0.39), 605 (80; 0.76), 690 (35; 0.81), 892 (60), 935 (10, dp), 991 (10, dp), 1145 (290; 0.50), 1196 (25), 1246 (30), 1301 (125; 0.45), 1400 (50), 1425 (25), 1629 (430; 0.20), 2907 (240; 0.17), 2930 (30), 2973 (90, dp), 2995 (140; 0.26), 3078 (40; 0.70).

*The spectrum of this substance was reported in [16] from data in [17]. The intensities found by us differ somewhat from those given in [16].

**In the case of $(CH_3)_3C - CH_2 - CH = CH_2$ we used the data in [17] on the degree of depolarization.

$$k = \frac{0{,}7787 \cdot 185}{84 \cdot 1{,}0337} = 1{,}66$$

IV. $CH_3Ge(CH_2 - CH = CH_2)_3$

177 (60), 292 (50), 381 (40), 402 (85; 0.45), 512 (165; 0.15), 539 (70; 0.75), 596 (95; 0.38), 688 (90; 0.73), 704 (60), 892 (27), 932 (30, dp), 990 (25, dp), 1145 (350, tw; 0.50), 1197 (35; 0.60), 1239 (45), 1301 (190; 0.30), 1398 (80; 0.50), 1426 (27), 1628 (540; 0.28), 2907 (200; 0.20), 2938 (95), 2976 (35), 2995 (230; 0.25), 3080 (50; 0.67).

$$k = \frac{0{,}7787 \cdot 211}{84 \cdot 1{,}0222} = 1{,}91$$

V. $(CH_3)_3SnCH_2 - CH = CH_2$

162 (320), 230 (45), 335 (5), 396 (70; 0.40), 482 (375; 0.27), 510 (1060; 0.17), 532 (720; 0.87), 671 (25), 882 (10), 930 (8, dp), 991 (6, dp), 1095 (640; 0.49), 1145 (30), 1192 (420, tw; 0.48), 1298 (130; 0.35), 1335 (10), 1375 (5), 1398 (60; 0.6), 1420 (5), 1625 (675; 0.30), 2861 (30), 2912 (320; 0.28), 2988 (140), 3082 (30; 0.86).

$$k = \frac{0{,}7787 \cdot 205}{84 \cdot 1{,}2540} = 1{,}51$$

It was shown in [5, 18] that the following frequencies are characteristic of the allyl group linked to an Si atom: 410, 930, 990, 1155, 1300, 1395, 1630, 3000, and 3080 cm^{-1}.

TABLE 1. Characteristic Frequencies of the Allyl Group in Compounds of the Type $(CH_3)_3M - CH_2 - CH = CH_2$ (in cm^{-1})*

M	$\nu_{C=C}$	γ_{-C-C-C}	$\rho_{=CH_2}$
C	1640 (120; 0,2)	460 (16; 0,5)	929 (1,0)**
Si	1630 (210; 0,2)	410 (35; 0,4)	930 (4, dp)
Ge	1630 (350; 0,25)	400 (60; 0,3)	930 (6, dp)
Sn	1625 (1020; 0,3)	396 (105; 0,4)	930 (12, dp)

M	$\rho_{-CH=CH_2}$	β_{M-CH_2-}	$\beta_{-CH-C<}$
C	991 (5, dp)		1288 (65; 0,46)**
Si	990 (5, dp)	1155 (110; 0,4)	1300 (100; 0,3)
Ge	990 (6, dp)	1145 (390; 0,5)	1300 (100; 0,3)
Sn	990 (8, dp)	1095 (960; 0,5)	1298 (200; 0,35)

M	α_{-CH_2}	ν_{CH} (symm. in $CH=CH_2$ group)	ν_{CH} (antisymm. in $=CH_2$ group)
C	1410 (35; 0,56)	3000 (70; 0,2)	3080 (35; 0,86)
Si	1395 (30; 0,6)	3000 (110; 0,2)	3078 (35; 0,8)
Ge	1398 (85; 0,6)	2994 (110; 0,25)	3080 (35; 0,8)
Sn	1398 (90; 0,6)	2988 (210)**	3082 (45; 0,86)

*The first number in parentheses is the line maximum intensity calculated for an equal number of molecules in the scattering volume; the second is the degree of depolarization.

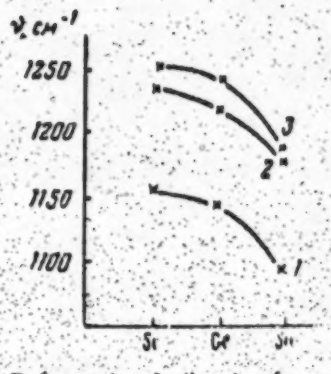
**Superposition of two lines.

According to Table 1, these Raman lines behave differently when Si is replaced by other group IV elements. Some (930, 990, 1300, 1398, and 3080 cm^{-1}) do not change their positions in the transition from C to Sn, while their intensities slowly increase. Therefore it may be concluded that these lines refer to those vibrations of the $-CH=CH_2$ end group, fairly distant from M, which are influenced little by the nature of the M atom. However, the frequency of the symmetrical CH valence vibration of the $CH_2=$ group, approximately 3000 cm^{-1} in the spectra of $(CH_3)_3C - CH_2 - CH = CH_2$ and $(CH_3)_3SiCH_2 - CH = CH_2$, unexpectedly falls in the case of $(CH_3)_3Ge\,CH_2 - CH = CH_2$ to 2994 cm^{-1}, while in the spectrum of $(CH_3)_3SnCH_2 - CH = CH_2$ the line probably coincides with the line corresponding to antisymmetrical CH valence vibration of the CH_2 group (2988 cm^{-1}).

An especially interesting fact is that the line corresponding to valence vibrations of the C = C double bond remains almost unchanged in position after substitution of the central atom, but its maximum intensity, as was stated earlier, increases approximately in the proportion of 1:2:4:8. Measurement of the integral intensity* of this line led to essentially the same result (after conversion to an equal number of molecules in the scattering volume):

$(CH_3)_3CCH_2 - CH = CH_2$ – 350;
$(CH_3)_3SiCH_2 - CH = CH_2$ – 620;
$(CH_3)_3GeCH_2 - CH = CH_2$ – 1170;
$(CH_3)_3SnCH_2 - CH = CH_2$ – 3020 u.

This shows that the half width of this line remains almost unchanged in the transition from C to Sn.



Deformational vibration frequencies of the M – C – H angle:

1) in $-M-CH_2-CH=CH_2$; 2) in $-M-C_2H_5$; 3) in $-M-CH_3$.

The line of frequency 1155 cm^{-1} in the spectrum of $(CH_3)_3SiCH_2 - CH = CH_2$ diminishes considerably in frequency and increases sharply in intensity when Si is replaced by Ge or Sn, and its half width increases appreciably; therefore, the intensity at the maximum is no longer a valid characteristic of this line. The integral intensity of this line (calculated for an equal number of molecules in the scattering volume) was found to be 440 units in the spectrum of $(CH_3)_3SiCH_2 - CH = CH_2$, 2400 units in the spectrum of $(CH_3)_3GeCH_2CH = CH_2$, and 9000 units in the spectrum of $(CH_3)_3SnCH_2 - CH = CH_2$. As reported earlier [3,6,19], this line is found only in the spectra of organosilicon compounds in which the Si atom is in the β-position to a double bond or an aromatic ring. The earlier assignment of this line [6, 18] was erroneous. We consider that it is more correct to assign it to deformational vibration of the M – C – H angle in the allyl group. This conclusion follows from a comparison of the positions of the frequencies of the vibration in question and of the vibration of the M – C – H angle in CH_3 and C_2H_5 groups attached to M (see figure). The similar variations of the frequencies of these vibrations on replacement of the central M atom indicates that they are of related origin. Variations of the vibration frequencies of the methyl groups are of the same character as for tetramethyl derivatives.

TABLE 2. Frequencies and Intensities of Valence Vibrations of the Skeletons of $(CH_3)_3M - CH_2 - CH = CH_2$ (where M = Si, Ge, Sn)*

Vibration type	Frequencies in cm^{-1}		
	Si	Ge	Sn
A_1^*	556 (220, 610; 0,18)	526 (250, 1050; 0,20)	482 (560, 3900; 0,27)
A_1^*	630 (100, 370; 0,15)	572 (450, 1320; 0,18)	510 (1600, 8700; 0,17)
E^*	609 (45, 275; 0,90)	600 (250, 1250; 1,0)	532 (1080, 5500; 0,87)

*The first number in parentheses represents the line maximum intensity; the second is the integral intensity; the third is the degree of depolarization.

Molecules of the $(CH_3)_3M - CH_2 - CH = CH_2$ type can be approximately regarded as belonging to the C_{3V} point symmetry group. Such a system has two symmetrical valence vibrations of the skeleton of type A_1, and one doubly degenerate vibration of type E.

Table 2 contains the frequencies, intensities calculated for an equal number of molecules in the scattering volume (both at the maximum and the integral values, because the lines alter appreciably in half width), and the degree of depolarization of the lines corresponding to valence vibrations of the skeletons of the molecules studied.

*The integral intensity was measured with the ISP-51 instrument with an FEP-1 attachment as described in [16], and expressed on the cyclohexane scale (the integral intensity of the cyclohexane 802 cm^{-1} line was taken as 500 units).

It is noteworthy that in the Si → Sn transition the increase of the intensity of the A_1' line is slower than of the A_1'' and E lines. This is probably because vibrations of types A_1'' and E occur with predominant change of the M – C_{methyl} coordinates in the $-M(CH_3)_3$ system, whereas the type A'_1 vibration occurs with predominant change of the M – C_{allyl} coordinate in $-M-CH_2-CH=CH_2$. Evidence for this is provided both by calculation of the frequencies of the skeleton of the $(CH_3)_3Si-CH_2-CH=CH_2$ molecule [5] and by the change in the integral intensity of the line corresponding to A_1'-type vibration in the Si → Sn transition, which is of the same character as for the line corresponding to vibration of the C = C double bond. This last fact may be some indication of interaction of the electron clouds of the M – C_{allyl} and C = C bonds (compare the double bond conjugation effect).

TABLE 3. Intensities per Allyl Group in Spectra of $(CH_3)_n Ge(CH_2-CH=CH_2)_{4-n}$ (n = 3, 2, 1)

Frequency in cm^{-1}	Line intensities divided by the number of allyl groups in molecule		
	$(CH_3)_3GeCH_2CH=CH_2$	$(CH_3)_2Ge(CH_2CH=CH_2)_2$	$CH_3Ge(CH_2-CH=CH_2)_3$
900	60	50	53
1193	15	20	23
1300	100	105	120
1395	35	42	50
1630	370	355	345
2900	110	115	140
2980	35	32	31

TABLE 4. Frequencies of Methylallyl Germane Skeletons

Symmetry	T_d	C_{3v}	C_{2v}	C_{3v}
Compound	$(CH_3)_3Ge$	$(CH_3)_2GeCH_2-CH=CH_2$	$(CH_3)_2Ge(CH_2-CH=CH_2)_2$	$(CH_3)Ge(CH_2-CH=CH_2)_3$
Frequency, cm^{-1}	A_1 558 (p) →	A_1 526 (0,20) →	A_1 521 (0,25) →	A_1 512 (0,15)
			B_1 537 (0,73) →	E 539 (0,76)
		A_1 572 (0,18) →	A_1 585 (0,39) →	A_1 596 (0,38)
	F_2 595 (dp) →	E 600 (1,0) →	B_2 605 (0,76)	

In general, in the C → Sn series we should expect an increase in the intensities of the lines corresponding to vibrations involving the central M atom, because an increase of the metallic properties of the central atom is associated with greater mobility of its outer electrons. The small change in the intensities of the lines corresponding to vibrations of bonds and angles distant from M is not surprising either. However, the unexpected increase in the intensity of the line corresponding to vibrations of the double bond in the spectra of allyl compounds, and the decrease in the intensity of the same line in the spectra of vinyl compounds in the transition from C to Sn, cannot be explained merely by increased polarizability of M; additional hypotheses are required to explain these facts. One such hypothesis is that mentioned earlier, concerning special interaction of the electron shell of the M atom (M = = Si, Ge, Sn) with the double bond, put forward in the course of our studies of organosilicon compounds. If the M atom is in the β-position to the double bond, then, as was stated earlier, this interaction is analogous in its manifestations to conjugation of double bonds. When Si is replaced by Ge or Sn this interaction is evidently intensified; this follows, for example, from a consideration of the relative intensities of the lines corresponding to double-bond vibrations in the spectra of allyl and vinyl compounds, $I(C=C)_{allyl}/I(C=C)_{vinyl}$; this ratio is 4.2 for Si, 11.2 for Ge, and 37.9 for Sn.

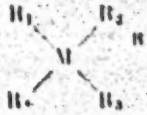
Without calculation of the vibration forms of the molecules it is difficult to suggest definite causes for this effect, but there is no doubt that a considerable part is played by the presence of vacant d-orbitals in Si, Ge, and Sn atoms (in contrast to C); in the opinion of several authors [20-22] such orbitals may even be involved in chemical bonding.

In order to confirm the "barrier" character of the central atom, and the consequent additive properties of the Raman spectrum, we obtained the spectra of $(CH_3)_2Ge(CH_2-CH=CH_2)_2$ and $CH_3Ge(CH_2-CH=CH_2)_3$. It was found that the frequencies characteristic of the $-CH_2-CH=CH_2$ group attached to Ge remained unchanged in position, while the intensities of these lines were doubled and trebled, respectively, as is the case for allyl silanes. This is illustrated in Table 3, which contains the line intensities (calculated for equal numbers of molecules in the scattering volume) divided by the number of allyl groups in the molecule.

The spectra of allyl germanes give an indication of the changes in the frequencies of the skeleton (see Table 4) with changes in the symmetry of the molecule as follows:

$$(CH_3)_4Ge \quad (T_d) \quad \rightarrow \quad (CH_3)_3Ge-CH_2-CH=CH_2 \quad (C_{3v}) \quad \rightarrow \quad (CH_3)_2Ge(CH_2-CH=CH_2)_2 \quad (C_{2v})$$

$$\rightarrow \quad CH_3Ge(CH_2-CH=CH_2)_3 \quad (C_{3v})$$

Thus, the following general conclusion may be drawn from a consideration of the spectra of organosilicon, organogermanium, and organotin compounds reported in the literature and determined by us. As the central M atom in the  molecule is replaced in the sequence C → Si → Ge → Sn, interaction between the R substituents weakens while interaction of bonds within each R group with the electron sheel of the central atom intensifies.

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APPLICATION OF INFRARED SPECTROSCOPY TO STUDIES OF THE STRUCTURE OF CERTAIN COMPLEX COMPOUNDS

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 569-572, September-October, 1961
Original article submitted February 16, 1961

Specific features of the application of infrared spectroscopy to studies of the structure of complex compounds are discussed. Typical applications of theoretical analysis of vibrations of multiatomic molecules to investigations of carbonyl and ethylene complexes of platinum are considered.

One of the commonest methods for studying molecular structure at the present time is investigation of the frequencies and forms of molecular vibrations with the aid of infrared and Raman spectra. The use of infrared spectroscopy in the chemistry of complex compounds is very promising because of the relatively simple experimental technique, the weak action of low-energy quanta on the substance studied, and the high sensitivity of vibration spectra to any changes in the ligand in complex formation. However, the vibration spectrum reflects the internal structure of molecules only indirectly, and depends in a fairly complex manner on geometrical and force characteristics. Therefore, considerable caution must be used in drawing conclusions from the experimental data. The position is made more complicated in the spectroscopy of complex compounds because the available experimental data are meager and unsystematic, a range of characteristic frequencies is not available, and in most cases it is impossible to record spectra below 400 cm^{-1}. This last fact often makes it impossible to observe frequencies corresponding to vibrations of metal – ligand bonds.

One possible way of overcoming the difficulties associated with interpretation of the observed absorption bands is by mathematical analysis of the vibration frequencies, and even of band intensities on the basis of the general theory of vibration spectra of multiatomic molecules. Of course, such work involves the application of modern computer techniques. However, this is probably the only way of solving many problems. At the same time it is premature, in absence of comparative data, to attempt to utilize numerical values of the force constants for judging bond character.

In this communication we give two examples of the application of the above-mentioned theoretical methods to studies of cis and trans $[CONH_3Cl_2Pt]$ and $K(C_2H_4PtCl_3) \cdot H_2O$; there is no agreed opinion in the literature concerning the character of CO and C_2H_4 bonding in these compounds, which are of considerable interest, in particular, in relation to the problem of the catalytic action of platinum.

Experimental values of the frequencies of infrared absorption bands for these compounds are given in [1-8]. In the present communication we deal only with interpretation of the spectra based only on theoretical analysis of the vibrations, and with conclusions drawn from this interpretation with regard to the structure of the complexes. All the necessary calculations were performed with the "Strela" electronic computer, programmed by A. M. Bogomolov.

Theoretical analysis of the vibrations of a planar model of the trans isomer (for fuller details, see [8]) was carried out in order to explain the observed spectra of carbonyl compounds. As a result, the following frequencies were assigned to vibrations of the OCPt group: 2062 cm^{-1} (CO valence vibration), 532 cm^{-1} (out-of-plane deformational vibration of the OCPt angle), and 477 cm^{-1} (in-plane deformational vibration of the OCPt angle) for the trans isomer, and corresponding frequencies of 2060, 534, and 483 cm^{-1} for the cis isomer.

Analysis showed that the valence vibration of the CO group in the complex is highly characteristic in frequency and form, and that the decrease of the frequency in comparison with the free CO molecule is due to slight weakening of the force constant for CO as the result of complex formation. This fact, and also the existence of two close frequencies in the 530-470 cm^{-1} region, assigned to deformational vibrations, indicates that the CO molecule is

attached linearly to platinum and that the electron cloud of carbon monoxide undergoes only small deformations. Such deformation is probably due to a certain degree of interaction of the unshared pair of electrons from CO with the free d-electrons of platinum.

Frequency in cm^{-1}, and intensity	Symmetry type	Assignment of frequencies
3081, v. w.	A_1	C – H valence vibrations
3013, v. w.	B_1	The same
2985, v. w.	B_2	The same
1505, w.	A_1	Deformational vibrations of HCH and HCC angles
1428, s.	B_1	The same
1241, w.	B_2	The same
1181, w.	A_1	Valence vibrations of C – C bond and deformational vibrations of HCH and HCC angles
1022, s.	B_1	Deformational vibration of removal of CH_2 groups out of the C_2H_4 plane
1010, s.	B_2	Rotation of CH_2 groups about the direction of the C – C bond
974, w.	A_1	Deformational vibration of removal of CH_2 groups out of the C_2H_4 plane
714, m.	B_1	Vibration of the C_2Pt triangle associated with stretching of C – Pt bonds
632, w.	A_1	The same

Let us now consider the compound of ethylene with platinum. Conclusions concerning the character of ethylene addition to Pt and the behavior of the C = C double bond during complex formation can be drawn from available x-ray data and infrared spectra [1-7, 9, 10]. According to these data, the ethylene molecule in the complex is perpendicular and symmetrical with respect to the $PtCl_3$ plane; this leads to the conclusion that the bond with Pt is effected through carbon atoms which are equivalent in this instance. The length of the C – C bond in the complex is 1.48 A. This suggests that the C – C bond becomes of the single type as the result of complex formation. We now pass to analysis of the infrared spectrum of this compound. It is known that ethylene forms a stable complex with Pt; therefore, regardless of the hypothesis about the behavior of the C – C bond in the complex, the presence of a stably bonded C_2H_4 group must inevitably lead to substantial changes in the spectrum by comparison with pure ethylene, both because of possible changes in the ethylene molecule itself and because of kinematic and dynamic interaction of vibrations of the ethylene molecule with C – Pt bonds.

Moreover, the C – C vibration in the complex must inevitably be accompanied by rotation of the C – Pt bonds, which may influence both the frequency and the intensity of this vibration. Therefore, the most logical procedure is to compare the spectrum of the complex with the spectra of such compounds as ethylene sulfide, ethylenimine, etc. This was done independently and simultaneously by us and by the foreign workers Powell and Sheppard [5]. However, the latter, in contrast to us, concluded that the C = C double bond remains unchanged when ethylene enters the complex. This shows that on the basis of comparative data alone it is impossible to assign frequencies conclusively and, hence, to draw unequivocal conclusions concerning the character of the bond in the complex. The sole basis of a correct interpretation of the observed spectrum can be complete theoretical analysis of the vibration frequencies and forms of the complex. We therefore carried out this type of investigation.

The model chosen was the C_2H_4Pt group, because Cl atoms have no appreciable influence on the vibrations of the part of the complex with which we are concerned. It was assumed that the CH_2 groups are unchanged during complex formation. This is justified by the retention of the CH valence frequencies and of the internal deformational frequencies of the HCH angle. It was further assumed that all the atoms of ethylene in the complex lie in the same plane. In reality the CH_2 groups in the complex apparently deviate somewhat from the plane of the C – C bond. However, the extent of this deviation is small and it was therefore disregarded in order to simplify the calculations. The geometrical parameters of the C_2Pt triangle were taken from [9]. Right from the start we did not attempt to calculate the spectrum exactly, as this is obviously impossible, first, because of the imprecision of the complex model and, second, because of the inevitable arbitrariness in the selection of the matrix of the potential energy constants. Therefore, all that could be done was to elucidate the general character of the spectral

manifestations of the vibrations of the complex, the extent to which different coordinates are involved in the vibrations, and the dependence of the frequencies on various elements in the force-constant matrix. On the basis of such analysis it is possible to assign the observed frequencies with adequate justification and to draw conclusions concerning the nature of the metal–ligand bond in the complex.

For analysis of the vibration frequencies and forms, secular equations were compiled and solved for all the symmetry types active in infrared absorption. More than 40 variants of force-constant matrices were investigated. As a result, the frequencies were assigned as shown in the table.

The force constants of the C – C and C – Pt bonds were found to be 4.5 and 3.0 · 10^5 dynes/cm, respectively.

All the frequencies were assigned in accordance with the greatest influence of the corresponding force constants (both diagonal and the most important nondiagonal), and with the calculated form of vibrations. In addition, a knowledge of the form of vibrations made it possible to draw certain conclusions concerning the intensities of the absorption bands, and this was also used for refinement of the proposed interpretation. It may be noted that, apart from the CH valence vibrations and (although to a lesser extent) the vibrations in the 1000 cm^{-1} region, none of the vibrations is characteristic in form and all the coordinates are involved in them to some extent.

The vibration associated to the greatest extent with stretching of the C – C bond (1181 cm^{-1}) is accompanied by simultaneous large changes in the HCH and HCC angles; these are of the same magnitude as the change in the bond itself. This frequency depends to a considerable extent on the diagonal force constants of the HCC and HCPt angles. This fact reduces to a considerable extent the precision of the determination of the C – C force constant. Stretching of the C – C bond also occurs at the vibration of 1505 cm^{-1} frequency, where its contribution reaches 30% of the change in the HCH angle. Moreover, this frequency depends considerably on the force constant of the C – C bond, so that it is higher than in free ethylene. If we assume that, with reasonable values of all the other constants, the magnitude of the elastic constant of the C – C bond is close to that for free ethylene, then the frequency in question should appear in the region above 1700 cm^{-1}, which is in complete contradiction to the experimental data.

The other deformational vibrations are of less interest to us and we shall not consider them in detail. We must only point out that the 1428 cm^{-1} band (B_1) should be entirely independent of the force constant; this accounts for its proximity to the corresponding frequency in free ethylene. Vibrations of the B_2 type should be independent of the C – C and C – Pt force constants. It is evident that the greatest changes should occur in the frequencies associated with rotation of the CH_2 groups about the C – C bond and removal of these groups from the ethylene plane, as elastic forces preventing changes of the HCPt angles arise during complex formation. It is clear from a comparison of the spectra of ethylene and the complex that considerable changes do in fact occur in the regions corresponding to nonplanar and rotational vibrations of free ethylene.

For elucidation of the nature of the carbon–platinum bond, we studied [8] the spectra of Pt complexes containing methyl groups: $[(CH_3)_3PtI]$ and $[(CH_3)_2(NH_3)_2Pt]I$, where the C – Pt bond is known to be covalent. The corresponding C – Pt force constant was found to be 2.9 · 10^5 dynes/cm. The similarity of the force constants for the methyl and ethylene complexes, and the fact that the equilibrium C – C distance and the corresponding force constant are of magnitudes characteristic of the single C – C bond, lead to the conclusion that valence electrons of the carbon atom play an important part in the formation of ethylene–platinum bonds. However, the distribution of these electrons in the methyl and ethylene complexes must be somewhat different, because in the latter case the electrons are in the field of three nuclei. This may account for the difference between the stabilities of the two compounds. Be that as it may, the physical properties of the C – C bond in the complex are close to those of a single bond. Similar behavior of the C – C double bond was observed by Eischens in a study of the adsorption of ethylene on platinum [11].

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THE STRUCTURE OF THE $Cu_{18}Si_4$ TYPE

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 573-577, September-October, 1961
Original article submitted April 12, 1960

Coordination of atoms in structures of the $Cu_{18}Si_4$ type is considered. The structure belongs to the class of closest packings of atoms of unequal size; it may be represented as a packing of deformed $[SiCu_3^{(1)}Cu_9^{(2)}]$ icosahedrons.

The $Cu_{18}Si_4$ structural type includes the compounds $Cu_{18}Si_4$ [1] and $Na_{18}Pb_4$ [2], and also $Li_{18}Ge_4$, the structure of which was recently determined by us [3]. In view of the discovery of a new compound with a structure of the $Cu_{18}Si_4$ type and the lack of a complete description of the latter in the literature, we consider it appropriate to examine this structural type in detail.

The $Cu_{18}Si_4$ structural type was discovered by Morral and Westgren [1]. In the $Cu_{18}Si_4$ structure the atoms occupy the following positions (space group $I\bar{4}3d - T_d^6$):

12 $Cu^{(1)}$ in 12 (a);
48 $Cu^{(2)}$ in 48 (e), x = 0.12, y = 0.16, z = 0.96;
16 Si in 16 (c), x = 0.208.

It is reported in [1] that each Si atom in the $Cu_{18}Si_4$ structure is on a threefold axis in the center of a triangle of $Cu^{(2)}$ atoms, the plane of which is perpendicular to the axis; $SiCu_3^{(2)}$ triangles alternate along the axis with $Cu_3^{(1)}$ triangles. More detailed descriptions of the $Cu_{18}Si_4$ structure have not been given.

Zintl and Harder [2], who found that $Na_{18}Pb_4$ has a structure of the $Cu_{18}Si_4$ type, report that the coordination polyhedron of the Pb atom (in the Si position) is similar to the polyhedron characteristic of hexagonal close packing ("hexagonal cube-octahedron") but is slightly deformed. The Pb atom is surrounded by 3 $Na^{(1)}$ and 3 + 3 + 3$Na^{(2)}$; The Pb – Na interatomic distances are given in full in [2]. The coordination characteristics of Na atoms are not given; only the distances between the Na atoms at the vertices of the polyhedron around Pb are indicated.

Strukturbericht [4] contains data from [1] and [2]; in addition, in the table of interatomic distances the neighbors of the $Cu^{(2)}$ atom are given as 1Si, 2 + 2$Cu^{(2)}$, and 1 + 1$Cu^{(1)}$.

No mention is made in any of the publications cited of the relation of the $Cu_{18}Si_4$ structural type to other types.

In order to describe the $Cu_{18}Si_4$ structural type and to determine its relation to other structural types, we must first know the nature of the coordination of all the atoms. The coordination polyhedron of the Si atom is represented in Fig. 1b and Fig. 2c. The vertices of the polyhedron contain 3$Cu^{(1)}$ and 9$Cu^{(2)}$; they lie along a threefold axis in the following sequence: $Cu_3^{(2)}$ (triangle), $Cu_3^{(1)}Cu_3^{(2)}$ (nonplanar hexagon), $Cu_3^{(2)}$. The $[SiCu_3^{(1)}Cu_9^{(2)}]$ polyhedron has $(3 - C_3)$ trigonal symmetry; it has 20 triangular faces, including 2 (bases) in the form of parallel equilateral $Cu_3^{(2)}$ triangles. The $Cu_3^{(1)}Cu_3^{(2)}$ hexagon divides this polyhedron into two halves. In one (upper in Fig. 1b) the faces are arranged similarly to a "hexagonal cube-octahedron" (Fig. 1a), with the difference that quadrilaterals close to squares but slightly broken along the diagonals correspond to the square faces of the latter. The second (lower) half differs from the first in that it has more strongly broken rhombuses instead of the almost plane squares; it resembles the half of the icosahedron in the β-Mn and Cr_3Si structural types (Fig. 1d, e). The $[SiCu_3^{(1)}Cu_9^{(2)}]$ polyhedron as a whole is intermediate between a "hexagonal cube-octahedron" and an icosahedron: in the "hexagonal cube-octahedron" (Fig. 1a) the sides of the bases are exactly under each other; in icosahedrons in the Cr_3Si and $MgZn_2$ structures (Fig. 1e, f) they are turned through 60°, in the icosahedron in the β-Mn structure (Fig. 1d) through 43°42', and in $[SiCu_3^{(1)}Cu_9^{(2)}]$ through 21°48'. Therefore, the $[SiCu_3^{(1)}Cu_9^{(2)}]$ polyhedron can be described as a twisted icosahedron.

Almost the same type of polyhedron (with a twist angle of 22°47') is formed around $Zn^{(4)}$ atoms in Mg_2Zn_{11}; it has been described as intermediate between a cube-octahedron and a normal 12-pointed polyhedron of the $CaZn_6$ type [5]. The twisted icosahedron, being a polyhedron without a center or planes of symmetry and without inversion axes, has two enantiomorphic modifications: the "left" (Fig. 1b) and the "right" (Fig. 1c). It is clear from Fig. 2c that both enter the structure of the $Cu_{15}Si_4$ type.

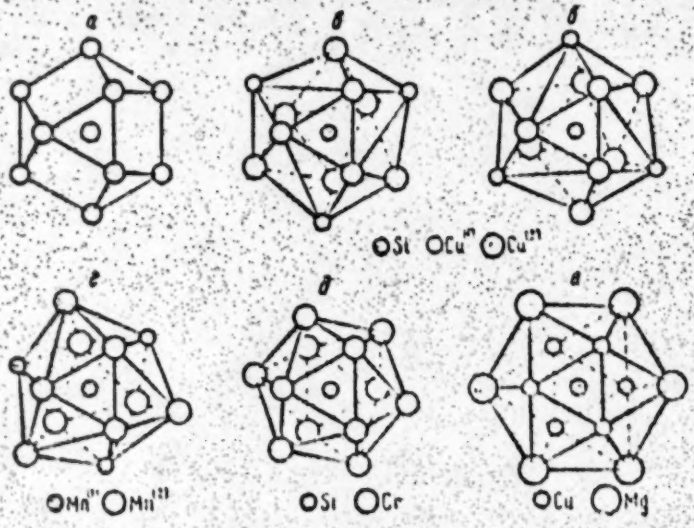

Fig. 1. Twelve-pointed polyhedrons in certain metallic structures (projections onto a plane perpendicular to the threefold axis): a) "hexagonal cube-octahedron" in the Mg structure; b) twisted $[SiCu_3^{(1)}Cu_9^{(2)}]$ icosahedron in the $Cu_{15}Si_4$ structure (left form); c) same polyhedron (right form); d) $[Mn_{(1)}Mn_3^{(1)}Mn_9^{(2)}]$ icosahedron in the β-Mn structure; e) "crystallographic" $[SiCr_{12}]$ icosahedron in the Cr_3Si structure; f) $[CuCu_6Mg_6]$ icosahedron in the $MgCu_2$ structure.

By analogy with the β-Mn and Cr_3Si structural types, in which some of the atoms have coordination number (CN) 12 (icosahedral coordination) and the others have CN 14 [6], it was to be expected that Cu atoms in $Cu_{15}Si_4$ (Li in $Li_{15}Ge_4$, Na in $Na_{15}Pb_4$) have CN not less than 12. This is quite probable, because (in the compounds $Li_{15}Ge_4$ and $Na_{15}Pb_4$) the atomic radii of Li and Na are greater than those of Ge and Pb, respectively. We determined the coordination numbers and the types of coordination polyhedrons of $Cu^{(1)}$ and $Cu^{(2)}$ atoms by calculation of the interatomic distances (see table) and with the aid of models. It was found that the $Cu^{(2)}$ atom has CN 13 and a coordination polyhedron of $1 - C_1$ symmetry with 22 triangular faces, of which 8 form four quadrilaterals slightly broken along the diagonals; the arrangement of the (1 + 5 + 6 + 1) vertices is similar to their arrangement in the polyhedron of the $Mn^{(3)}$ atom in the α-Mn structure [5]. The $Cu^{(1)}$ atom has CN 12 and a coordination polyhedron in the form of a deformed cube-octahedron ($\bar{4} - S_4$ symmetry; 20 triangular faces, 8 of which form four almost planar quadrilaterals; the arrangement of the vertices is 4 + 4 + 4) (Fig. 2a).

The presence of these polyhedrons in the $Cu_{15}Si_4$ structure indicates that the effective atomic radii in it are not equal; they diminish in the sequence $Cu^{(2)} - Cu^{(1)} - Si$. In accordance with the notation adopted by us for larger and smaller atoms [5], we denote the components of compounds of the $Cu_{15}Si_4$ type by the letters R (Cu, Li, Na) and X (Si, Ge, Pb).

In order to describe the $Cu_{15}Si_4$ structural type we must know not only the configurations of the coordination polyhedrons but also the manner in which they are joined. Since the Si atoms are surrounded by Cu atoms only, the twisted $[SiCu_3^{(1)}Cu_9^{(2)}]$ icosahedrons do not interpenetrate; hence, the structure can be described as a packing of these polyhedrons. In this respect the $Cu_{15}Si_4$ structure is similar to the structure of the Cr_3Si type, which contains $[SiCr_{12}]$ icosahedrons which do not interpenetrate, and differs from the β-Mn type of structure, in which the icosahedrons contain atoms of one kind both in the center and at the vertices.

In the Cr_3Si type of structure, the icosahedrons are so joined that each has eight faces in common with eight neighboring icosahedrons (distance between centers $D_1 = 0.866a$), and six edges in common with six more remote icosahedrons ($D_2 = a$), while each vertex belongs to four icosahedrons ($SiCr_3 = SiCr_{12}/_4$). The entire space of the structure may be regarded as composed of $[SiCr_{12}]$ icosahedrons (two per unit cell) and empty tetragonal Cr_4 tetrahedrons (six per unit cell) [7]; the latter are joined by their edges to form chains parallel to the X, Y, and Z axes. The centers of the tetrahedrons form a regular system of 6(d) points of the $Pm3n - O_h^3$ space group.

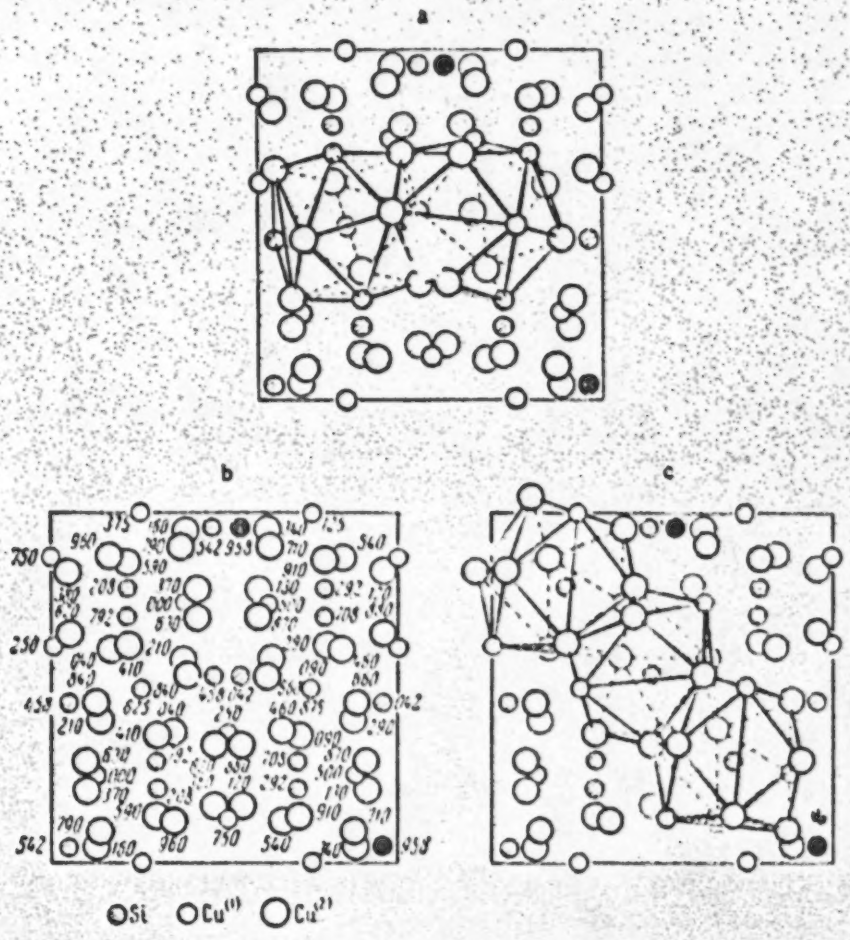

Fig. 2. Structure of the $Cu_{15}Si_4$ type (projections of the unit cell onto the xy plane): a) $[Cu^{(1)}Si_4Cu_8^{(2)}]$ and $[Cu^{(2)}Si_3Cu_2^{(1)}Cu_8^{(2)}]$ coordination polyhedrons; b) positions of the atoms (z coordinates in thousandths of a are given); c) joining of twisted $[SiCu_3^{(1)}Cu_9^{(2)}]$ icosahedrons along a threefold axis (left polyhedron in center, right polyhedrons at ends).

In the structure of the $Cu_{15}Si_4$ type the interconnection of the (twisted) icosahedrons is much more complex. The $Cu_{15}Si_4$ unit cell contains 16 twisted icosahedrons, including 8 of the "right" type in the positions (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) + + (x, x, x; x, $\bar{x}$, $\frac{1}{2} - x$;), and 8 of the "left" type with centers at (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) + ($\frac{1}{4} + x$, $\frac{1}{4} + x$, $\frac{1}{4} + x$; $\frac{1}{4} + x$, $\frac{1}{4} - x$, $\frac{3}{4} - x$;); $x = 0.208$. Each icosahedron is surrounded by 11 icosahedrons as nearest neighbors: two of opposite form (A), with common faces (equilateral triangles) with the central icosahedron and lying with it along the same threefold axis (the distance between the Si atoms, $d_2 = 0.434a$), three of the same form (B), having faces in common with the central icosahedron ($d_1 = 0.425a$), and six of the opposite form (C,D) with common edges ($d_3 = 0.447a$). The arrangement of the icosahedrons is shown in Fig. 3 (the central icosahedron is under the upper icosahedron A; the lower icosahedron A is identical to the upper). The centers of the icosahedrons are at the vertices of a coordination polyhedron characteristic of Hg atoms in UHg_2 (the trigonal prism B_2C_3 with two additional vertices A

against the bases and three vertices D against the side faces); in the structure of the $Cu_{15}Si_4$ type this polyhedron is deformed in such a manner that all the icosahedrons are surrounded similarly. The joining of the icosahedrons along the threefold axes (Fig. 2c) is the same as in the Cr_3Si structure, and differs from that in the β-Mn structure, in which there are octahedral cavities between certain pairs of icosahedrons [5]. Each $Cu^{(1)}$ atom at the vertex of the $[SiCu_3^{(1)}Cu_9^{(2)}]$ icosahedron belongs to four icosahedrons, and each $Cu^{(2)}$ atom to three $[Si_4Cu_3^{(1)}Cu_{12}^{(2)} = 4SiCu_{3/4}^{(1)}Cu_{9/3}^{(2)}]$.

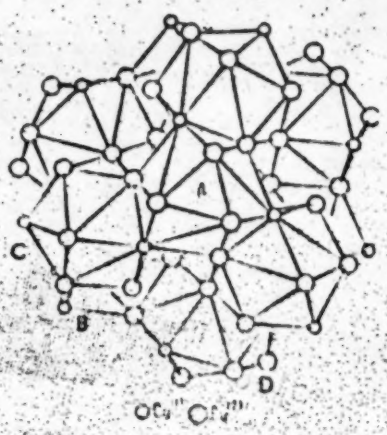

Fig. 3. Structure of the $Cu_{15}Si_4$ type as a packing of twisted $[SiCu_3^{(1)}Cu_9^{(2)}]$ icosahedrons (projection onto a plane perpendicular to the threefold axis).

In addition to the 11 icosahedrons surrounding each given icosahedrons as nearest neighbors, there are 15 icosahedrons (not in contact with the central one) at greater distances. Between each eight icosahedrons there are gaps ("cavities") in the form of elongated nonconvex 12-pointed polyhedrons situated along the fourfold axes. Each "cavity" consists of a very deformed twisted cube with its center in position 12 (b), for example, at $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, and, adjacent to this cube, of two very deformed trigonal prisms with its centers in positions 24 (d), for example, at $\frac{1}{2}$, $\frac{1}{4}$, x, and $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{4}$ + x, with $x \approx 0.06$. The distances between the centers and vertices of the "cavities" are too small for the "cavity" to accommodate atoms (the radius of an interstitial atom must be less than 0.3-0.4 A).

It follows from the foregoing that the $Cr_{15}Si_4$ structural type has features in common with the Cr_3Si_4 type (packing of icosahedrons, absence of large cavities) and with the following types: β-Mn (character

Interatomic Distances d and Coordination Numbers in Structures of the $Cu_{14}Si_4$ Type

Atoms	d	CN	Atoms	d	CN
X — $3R^{(2)}$	$d_1 = 0{,}245a$	12	$R^{(2)}$ — 1X	d_1	13
$3R^{(2)}$	$d_2 = 0{,}259a$		$1R^{(1)}$	d_2	
$3R^{(2)}$	$d_3 = 0{,}268a$		1X	d_3	
$3R^{(1)}$	$d_4 = 0{,}272a$		$2R^{(2)}$	$d_4 = 0{,}259\,a$	
$R^{(1)}$ — $4R^{(2)}$	$d_5 = 0{,}254a$		$1R^{(1)}$	d_5	
$4R^{(2)}$	$d_6 = 0{,}264a$		1X	d_6	
4X	d_7	12	$2R^{(2)}$	$d_7 = 0{,}272a$	
			$1R^{(2)}$	$d_8 = 0{,}272a$	
			$1R^{(2)}$	$d_{10} = 0{,}300a$	
			$2R^{(2)}$	$d_{11} = 0{,}306a$	

X = Si, Ge, Pb; R = Cu, Li, Na

of deformation of the icosahedron), α-Mn [CN 13 of $Cu^{(2)}$ atoms], Cu [cube-octahedral coordination of $Cu^{(1)}$ atoms], and Mg ($[SiCu_3^{(1)}Cu_9^{(2)}]$ polyhedron allied to the "hexagonal cube-octahedron"). In view of the coordination characteristics of the $Cu_{15}Si_4$ type, it should be assigned to the class of structural types with closest packing of atoms of unequal size and with high coordination numbers (CN ≥ 12). This structural type occupies the extreme position in the series of types with high CN (R_mX_n), as it has the highest content of large atoms R, corresponding to the formula $R_{15}X_4$, and the lowest CN of these atoms (13 and 12); up to now the extreme position has been assigned to the Cr_3Si type (R_3X) with CN (R) = 14 [5]. The ratio of atomic radii $k = r_R/r_X$ is close to 1.0 in compounds of the $Cu_{15}Si_4$ type, as in compounds of the Cr_3Si type. The average value of k, calculated from the values for the compounds $Cu_{15}Si_4$ (0.96), $Li_{15}Ge_4$ (1.11), and $Na_{15}Pb_4$ (1.08), is 1.05.

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X-RAY DIFFRACTION DETERMINATION OF THE HOMOGENEITY BOUNDARIES AND NATURE OF THE β-NiS PHASE

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 578-584, September-October, 1961
Original article submitted April 13, 1960.

Precision determinations of the constants of the hexagonal lattice of the β-NiS phase with the nickel arsenide structure for Ni – S alloys in the composition range from 47.81 to 55.33 atomic %S (after quenching at 450, 470, and 600°), showed that the homogeneity region of this phase lies in the range of 50.0-51.3% atomic % S. The lattice constants, pyenometric density, and number of atoms in the unit cell in the homogeneity region of the β-NiS phase all decrease with increase of the sulfur content in the solid solution, which indicates the formation of a subtractive nickel arsenide defect structure with vacancies in the nickel positions. This result was confirmed by measurements of reflection intensities by the ionization method.

In a study of the causes of fluctuations of the composition of hexagonal iron sulfide FeS, Hägg and Sucksdorff [1] found that the constants, and, therefore, the volume of the unit cell decrease with increasing sulfur content in solid Fe – S solutions. They assumed that an excess of sulfur above the stoichiometric FeS composition is obtained owing to the existence of vacancies at the positions of the iron atoms in the FeS lattice. Bieltz and co-workers [2] found that the high-temperature β-NiS phase, like FeS, has a relatively wide homogeneity region, in the range of 50.0-54.4% atomic % S. They assumed that some of the nickel atoms are removed as the sulfur content increases and vacant positions arise at the nickel positions in the β-NiS lattice.

Lundkvist [3], on the basis of x-ray diffraction data for the Ni – S system, confirmed that the cell volume of β-NiS decreases with increasing sulfur content but, in his opinion, this volume decrease is considerably less for β-NiS than for FeS. He calculated lattice constants for compositions quenched in the 400-680° range; for nickel-rich compositions the values were: a = 3.428, c = 5.340 kX, c/a = 1.553, V = 54.3 kX^3; and for compositions rich in sulfur, a = 3.420, c = 5.315 kX, c/a = 1.554, V = 53.8 kX^3. Lundkvist considers that the homogeneity region of β-NiS must be in the range of 51 atomic % S.

Rosenqvist [4] showed, in a thermodynamic study of nickel sulfides, that the monosulfide NiS_{1+x} exists at 400 and 510° in the range of 35.1-36.6 % S by weight (49.8-51.4 atomic % S).

In our first investigation [5], concerned with an x-ray phase study of the Ni – S system for compositions annealed for 72 hours at 450° and quenched in water at 0°, the homogeneity region of the β-NiS phase was found to lie in the range of 50.08-51.3 atomic % S in accordance with precision determinations of the lattice constants. The lattice constants were: for compositions rich in nickel, a = 3.432 ± 0.001; c = 5.340 ± 0.002 kX; c/a = 1.556; V = = 54.5 kX^3, and for compositions rich in sulfur, a = 3.421 ± 0.001, c = 5.309 ± 0.002 kX, c/a = 1.552, V = 53.8 kX^3. These results are in good agreement with Lundkvist's data [3].

In view of the fact that the type of solid solution in the homogeneity region of the β-NiS phase has not been determined experimentally, we undertook this task and investigated the presumed analogy between the structures of FeS and β-NiS solid solutions. A similar investigation was carried out simultaneously with ours by Laffitte and Benard [6,7], who investigated the boundaries of the homogeneity region of hexagonal nickel monosulfide in the 480-780° range by x-ray diffraction methods; they found that in this range the limit of the homogeneity region on the sulfur-rich side does not alter, and at 485° corresponds to the formula $Ni_{0.943}S$ (50.00-51.50 atomic % S). They also found that the homogeneity region narrows rapidly at temperatures above 780° and below 470°. By measurements of densities and lattice constants for compositions within the homogeneity region of β-NiS, annealed for 2.5

months at 600°, these workers also demonstrated the existence of vacancies at the positions of Ni atoms in the β-NiS lattice and concluded that a defect structure of the nickel arsenide type is formed in β-NiS solid solutions by subtraction of nickel atoms.

In distinction from Lafflitte and Benard, in our investigation of the nature of the solid solution we used the ionization method for recording intensities for a number of variants of the structure of the β-NiS phase in addition to calculating the number of atoms in the unit cell.

TABLE 1. Chemical and Phase Analyses of Nickel Sulfide Specimens Quenced at 450, 470, and 600°

% by weight		Atomic %		Quenching temp., °C	Phase composition
S	Ni	S	Ni		
33,18	66,82	47,58	52,42	450	β-NiS + Ni_6S_5
33,38	66,62	47,84	52,16	600	the same
34,25	65,75	48,81	51,19	450 and 470	» »
34,79	65,21	49,40	50,60	600	» »
35,27	64,73	49,93	50,07	600	β-NiS
35,50	64,50	50,18	49,82	470	the same
35,55	64,45	50,19	49,81	450 and 470	»
35,58	64,41	50,28	49,72	600	»
36,00	64,00	50,72	49,28	450 и 600	»
36,30	63,70	51,06	48,94	450	»
38,74	61,26	53,65	46,35	600	β-NiS + NiS_2
40,31	59,69	55,28	44,72	600	the same
41,39	58,70	56,29	43,71	450 и 470	» »
42,41	57,59	57,42	42,58	450	» »

Preparation of Alloys

Sulfide specimens containing 47.81-56.29 atomic % S were used in the quenched state for the investigation. The alloys were prepared by fusion of thoroughly mixed electrolytic nickel powder of 99.8% purity with powdered crystalline sulfur of 99.999% purity in quartz tubes sealed under vacuum (10^{-2} mm Hg). The powdered alloys were annealed for 72 hours at 450°, and for 120 hours at 470 and 600°, and quenched in water at 0°. All the alloys were analyzed chemically for sulfur and nickel by Z. V. Popova. The compositions of the specimens studied are given in Table 1.

Method of Investigation

The x-ray patterns of the specimens were obtained by the powder method with copper and iron radiation in cylindrical cameras 57.3 mm in diameter; the film was put in asymmetrically. Annealing at 450-600° for 120 hours was quite sufficient to remove the effects of work-hardening from powders made by grinding of the specimens in an agate mortar, and to give x-ray patterns with sharp $K\alpha_1$ and $K\alpha_2$ doublets. The x-ray patterns of these powders were suitable for precision determinations of lattice constants and for phase analysis.

The powder for the x-ray analysis was sifted through a fine screen and rolled onto a glass thread about 0.1 mm in diameter with the aid of collodion. The patterns were measured with a ruler between the centers of the lines with a precision of ± 0.1 mm for phase analysis of the specimens, and in the IZA-2 comparator with a precision of ± 0.03 to 0.04 mm for precision determinations of the lattice constants.

In calculations of the glide angles, a correction was applied for absorption. Line intensities were assessed visually on a nine-point scale. Phase analysis of the specimens was performed by comparison of the x-ray patterns with each other and with standard patterns corresponding to pure phases. The principal standards were the x-ray patterns of the following: the high-temperature NiS β-phase with structure of the NiAs type; the low-temperature NiS α-phase with rhombohedral structure of the millerite type; Ni_9S_8 with a close-packed hexagonal lattice (according to our preliminary data); Ni_6S_5 with rhombic structure; and NiS_2 with cubic structure of the pyrite type [5].

The constants of the hexagonal β-NiS lattice for our specimens were determined from lines with angles $\theta > 50°$, with extrapolation by Kettmann's method [8].

Densities were determined at 20 ± 0.1° by means of a pycnometer with a stopper and a capillary 1 mm in diameter (with toluene as the liquid). The error in the density determinations was less than 1% of the total value.

In order to confirm the type of solid β-NiS solid solution indicated by the x-ray data and density, and to determine the nature of the defects, we measured the reflection intensities by the ionization method for a composition with 36.0 wt.% S (50.72 atomic % S) from the homogeneity region of β-NiS quenched at 470°. This was done with copper radiation in the URS-50I ionization instrument with automatic recording of the reflection intensity curves. The relative intensities of the reflections from the 100, 002, 101, 102, 110, and 200 planes were determined (from the areas of the peaks corresponding to these planes on the ionization curve; two curves taken in succession were used). The 102 reflection intensity was taken as 100. The powdered specimen was packed in a Plexiglas capsule 10 mm in diameter and 0.5 mm high for the determination.

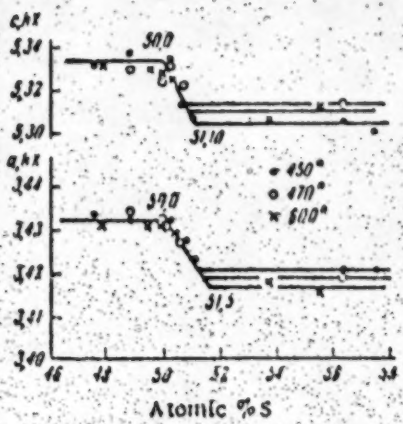

Fig. 1. Variations of the lattice constant of the β-NiS phase with composition and quenching temperature.

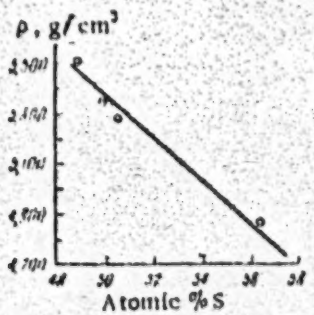

Fig. 2. Density variations of Ni – S specimens quenched at 470°.

The theoretical reflection intensities in relative units were calculated from the formula:

$$I = pL|F|^2,$$

where p is the multiplicity factor in the Debye method; L is the Lorentz and the polarization factor; $|F|^2$ is the structure factor, including the atomic factor. Since the ionization pattern was obtained from a specimen which was rotated through an angle half that of the counter, the absorption factor was ignored in the intensity calculations. The temperature factor was also disregarded.

Calculation of the structure factor $|F|^2$ was based on the known coordinates of sulfur and nickel atoms in the β-NiS lattice: Ni: 000, 001/2; S: 1/3 2/3 1/4; 2/3 1/3 3/4.

The number of Ni atoms in the unit cell, found experimentally for compositions from the homogeneity region of β-NiS, quenched at 470 and 600°, was compared with the value calculated theoretically from the formula

$$N_2 = \left(\frac{N_1 \cdot A_2}{A_1}\right) N_1 \cdot k / 1_1,$$

where N_2 is the number of Ni atoms in the unit cell; A_2 is the atomic % of Ni; A_1 is the atomic % of S; N_1 is the number of sulfur atoms in the unit cell, taken as two.

Results of the Investigation

Table 1 contains the results of chemical and phase analyses of nickel sulfide specimens quenched at 450, 470, and 600°. Table 2 gives the lattice constants of the β-NiS phase, the volumes of the unit cells calculated from these constants, the densities (found by the pycnometric method), and the numbers of atoms in the cell (experimental and calculated) for specimens quenched at 450, 470, and 600°.

The curves in Fig. 1 show variations of the cell constants of β-NiS with composition at 450, 470, and 600°. It follows from Fig. 1 and Table 2 that the cell constants a and c of the β-NiS phase decrease appreciably in the homogeneity region with increase of the sulfur content in the solid solution, whereas in the two-phase regions the constants remain unchanged.

The boundary of the homogeneity region of the β-NiS phase at the nickel-rich side is at 50.05 ± 0.05 atomic % S at all temperatures, which is virtually the stoichiometric NiS composition. The boundaries of the homogeneity region on the sulfur-rich side change little at 450, 470, and 600°, and correspond to the points of intersection of the cell constant-composition lines (in the two-phase β-NiS + NiS_2 region at the corresponding temperature) with the curve showing variations of the cell constants in the homogeneity region. These data are presented in Table 3.

Table 3 shows that the solubility of sulfur in β-NiS found from the change of a is greater than that found from the change of c, and also the solubility found from a increases slightly with temperature, whereas that found from c

falls somewhat. The average solubility of sulfur in β-NiS as found from a and c remains almost unchanged in the 450-600° range, and the boundary lies at 51.13 ± 0.06 atomic % S. It should be pointed out, however, that a was determined with higher precision than c, and the values for a are less scattered. Therefore, the solubility boundary of sulfur in β-NiS should be closer to the data found from changes of a than of c. The maximum solubility at 600° is at 51.5 atomic % S, and at 450° at 51.2 atomic % S, which is in good agreement with the data of Laffitte and Benard [6,7].

TABLE 2. Variations of the Cell Constants of the β-NiS Phase, Density (ρ), Volume (V), and Number of Atoms in the Cell with Sulfur Concentration in Specimens Quenched at 450, 470, and 600°

At. % S	Quenching temp., °C	a, Å	c, Å	c/a	V, Å³	ρ, g/cm³	No. of atoms in cell	
							expt.	calc.
47,58	450	3,433	5,337	1,555	—	—	—	—
47,84	600	3,432	5,337	1,555	54,4	5,49	—	—
48,81	450	3,432	5,342	1,556	—	—	—	—
48,81	470	3,433	5,335	1,554	54,5	5,53	—	—
49,40	600	3,431	5,330	1,555	54,4	5,46	—	—
49,93	600	3,431	5,334	1,555	54,4	5,44	3,95	4,00
50,18	470	3,432	5,331	1,553	54,4	5,37	3,90	3,98
50,19	450	3,432	5,340	1,556	—	—	—	—
50,19	470	3,430	5,321	1,555	54,2	5,37	3,89	3,98
50,28	600	3,430	5,330	1,554	54,3	5,34	3,88	3,95
50,72	450	3,425	5,319	1,552	—	—	—	—
50,72	470	3,427	5,321	1,553	54,0	5,32	3,86	3,94
51,06	450	3,422	5,312	1,552	—	—	—	—
53,65	600	3,418	5,312	1,554	53,8	5,22	—	—
55,28	600	3,419	5,318	1,557	53,8	4,85	—	—
56,29	450	3,421	5,311	1,553	—	—	—	—
56,29	470	3,419	5,318	1,555	53,8	5,11	—	—
57,42	450	3,421	5,307	1,551	—	—	—	—

The curve in Fig. 2, based on the data in Table 2, represents the density variations of specimens quenched at 470°; the density of specimens quenched at 600° varies in exactly the same manner. Increase of the sulfur concentration in the β-NiS solid solution diminishes the lattice constants, unit cell volume, and density. The number of atoms N in the unit cell decreases with increase of sulfur concentration; the composition with 50.72 atomic % S quenched at 470°, N = 3.86; for the composition with 50.28 atomic % S quenched at 600°, N = 3.88 (i.e., appreciably less than for the exact stoichiometric composition, when N = 3.95).

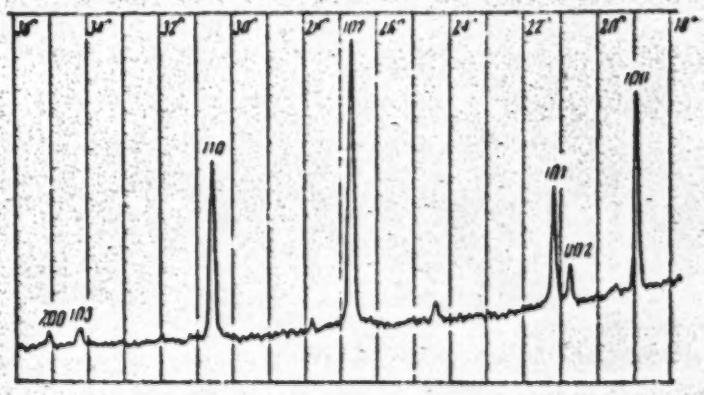

Fig. 3. Ionization curve of reflection intensities for the composition with 36.0% S by weight (50.72 atomic % S).

The only possible explanation of these facts is that in the 450-600° range the β-phase of NiS is a defect solid solution with a deficiency of nickel atoms, analogous to the iron-deficient solid solution of sulfur in FeS studied by Hägg.

This conclusion was confirmed by a determination of the reflection intensities by the ionization method for a specimen with 36.0% sulfur by weight (50.72 atomic % S) quenched at 470°. The ionization curve is shown in Fig. 3. Table 4 and Fig. 4 contain the results of determinations of the relative intensities of the reflections from the areas of the peaks of the ionization curves. For comparison, we calculated the following variants of the reflection intensities in relation to the arrangement of the defects in the β-NiS lattice.

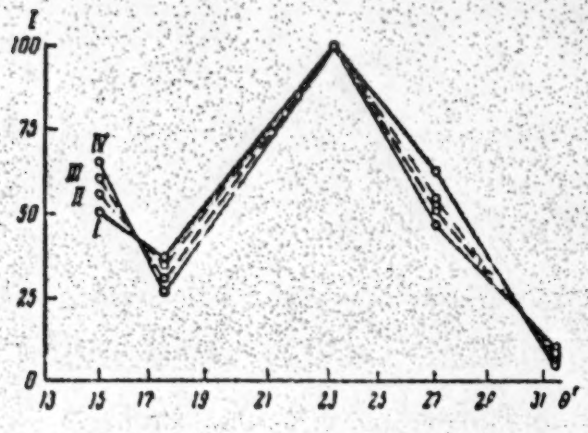

Fig. 4. β-NiS reflection intensity curves for a composition with 50.72 atomic % S: I) experimental curve; II), III), and IV) curves calculated with various assumptions (explanation in text).

TABLE 3. Boundary of the Homogeneity Region of β-NiS in atomic % S on the Sulfur-Rich Side

Quenching temperature, °C	Boundary of homogeneity curve from change of a	from change of c	average
450	51.2	51.1	51.15
470	51.3	50.8	51.05
600	51.5	50.9	51.20

1. The total number of atoms in the β-NiS unit cell, in agreement with the experimental value, is 3.86. The defects (vacancies) are present at the positions of the nickel atoms and are distributed statistically (curve II). It is immaterial for any of the planes with the exception of 101 whether the defect is in the position of a nickel atom with 0, 0, 0 or 0, 0, ½ coordinates. For the 101 plane the intensity calculated on the assumption that the defect is in the position of a nickel atom with coordinates 0, 0, 0 is 48.1; for the defect in the position of a nickel atom with coordinates 0, 0, ½, the intensity is 25.6. Both these values differ considerably from the experimental intensity and from the intensity calculated for a statistical distribution of defects in the β-NiS lattice (36.0 and 36.5).

2. The total number of atoms in the β-NiS unit cell, in agreement with the theoretical value calculated from the results of chemical analysis, is 3.94 (2S + 1.94 Ni). The defects are vacancies at the positions of the nickel atoms (curve III).

3. There are no defects in the β-NiS lattice. The total number of atoms in the unit cell is 4: 2Ni + 2S (curve IV).

The experimental intensities are compared with the calculated values for all these variants in Table 4. The intensity curves in Fig. 4 are plotted from these data. It follows from Table 4 and Fig. 4 that the best agreement with the experimental intensities (curve I) is given by the intensities calculated on the assumption that the defects in the β-NiS lattice are statistically distributed, with the experimental value of 3.86 for the number of atoms in the unit cell (curve II). These calculated intensities therefore confirm our conclusion that nickel sulfide specimens in the homogeneity region of β-NiS are defect solid solutions deficient in nickel atoms.

TABLE 4. Comparison of Experimental and Calculated Intensities for Various Arrangements of Defects in the β-NiS Lattice (composition with 50.72 atomic % S, quenched at 470°; CuK_α radiation used in the ionization instrument)

hkl	$I_{meas.}$, relative units	$I_{calc.}$, relative units		
		variant 1, curve II	variant 2, curve III	variant 3, curve IV
100	51,2	60,6	63,7	65,9
002	8,2	5,3	5,9	6,4
101	36,5	36,0	33,8	32,1
102	100	100	100	100
110	62,8	48,4	47,9	47,4
200	5,4	5,6	5,9	6,1

For elucidation of the type of bonding between sulfur and nickel atoms in the defect β-NiS lattice, we calculated the interatomic distances for two compositions, with 50.19 and 50.72 atomic % S, and compared them with the sums of the covalent and ionic radii of nickel and sulfur for coordination number 6 (Table 5).

TABLE 5. Measured Interatomic Distances (meas) and Sums of the Covalent (cov) and Ionic (ion) Radii in kX

Composition	Ni – S			S – S			Ni – Ni		
	meas.	cov.	ion	meas.	cov.	ion	meas.	cov.	ion
$Ni_{0.992}S$	2,39	2,50 II 2,42 III	2,52	3,43	2,22	3,48	2,98	2,78 II 2,62 III	1,56
$Ni_{0.972}S$	2,38			3,42			2,65		

Goldschmidt's values [9] of the ionic radii $r_{Ni^{2+}} = 0.78$ and $r_{S^{2-}} = 1.74$ kX were used; the octahedral covalent radii of nickel were taken from the paper by Pauling and Huggins [9,10]; for bivalent nickel, $r_{NiII} = 1.39$ and for trivalent nickel $r_{NiIII} = 1.31$ kX. Only the tetrahedral covalent radius, 1.04 kX, is known for sulfur. For the octahedral covalent radius of sulfur we took the value 1.11 kX, obtained after the tetrahedral radius has been increased by 7% when the coordination number changes from 4 to 6, in accordance with the Laves correction curve [9, 11].

It follows from Table 5 that the experimental values of the Ni – S interatomic distances are closer to the sum of the covalent radii of trivalent nickel (2.42 III) and sulfur than to the sum of the covalent radii of bivalent nickel (2.50 II) and sulfur. The sum of the ionic radii deviates even more from the experimental distances. From this it may be concluded that covalent bonds predominate in the β-NiS lattice. According to our preliminary data, the electrical conductance of β-NiS is of the semimetallic type; this indicates that metallic bonds are present in addition to covalent.

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X-RAY INVESTIGATION OF POTASSIUM POLYURANATES

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 585-590, September-October 1961
Original article submitted May 2, 1960

Potassium uranates of the formula $K_2O \cdot 3.1\text{-}6.0\ UO_3$ constitute a phase of variable composition, the structure of which contains infinite hexagonal uranyl–oxygen layers $(UO_2)O_3$. The potassium atoms and some of the uranium atoms are situated between the layers and bind them together. Rhombic distortion of this structure is sometimes observed in uranates of the formula $K_2O \cdot 5\text{-}6\ UO_3$. Hydrated potassium polyuranates are of similar structure and their composition should be represented by the formula $(K, H_2O)UO_2(O, OH)_2 \cdot nH_2O$. Variations of the composition of hydrated polyuranates are associated with changes in the oxygen–hydroxyl ratio in the uranyl–oxygen motif.

The determining element of uranate structures is the particular type of the uranyl–oxygen motif [1]. In the simplest cases the symmetry and parameters of the uranyl–oxygen motif (chain or layer) coincide with the symmetry and some of the parameters of the uranate unit cell. Sometimes the symmetry of the uranyl–oxygen motif is lowered under the influence of cations [1,2]. Such simple relationships are hardly to be expected in polyuranates of more complex structure. Uranium atoms have the main influence on the reflection intensities of uranates (with the exception of heavy-metal uranates). Therefore, if the uranium atoms are arranged in accordance with a relatively simple law, it is possible to isolate a subcell associated only with the relative arrangement of the uranium atoms. Having determined this subcell, we can establish the type of the uranyl–oxygen motif. This reasoning is applied in the present paper to potassium polyuranates.

TABLE 1. Phase Analysis of Potassium Polyuranates

$K_2O:UO_3$ ratio	Phase composition*	$K_2O:UO_3$ ratio	Phase composition*
1:2.5	$K_2U_2O_7$ + tri-hexauranate (H)	1:4.1	tri-hexauranate (H)
1:2.8	The same	1:5	The same
1:2.9	The same	1:5 (600°)	tri-hexauranate (R)
1:3.0	The same	1:5.3	tri-hexauranate (H)
1:3.1	tri-hexauranate (R)	1:5.65	tri-hexauranate (R)
1:3.2	The same	1:6	tri-hexauranate (H)**
1:3.4	The same	1:7.1	tri-hexauranate (R) + U_3O_8
1:3.6	The same	1:10	The same

*H = hexagonal phase; R = rhombic phase.

**The specimen of this composition contained individual inclusions of U_3O_8 after calcination at 800°, but no lines of this oxide were present in the x-ray patterns.

The powder method was used for studying potassium polyuranates.* RKD-57 cameras with CuK radiation (sometimes with an Ni filter) were used. The line intensities were estimated visually with the aid of the ratio of I_α to I_β (which was taken as 5:1 for convenience in construction of the scale, instead of the true value of 7.5:1). The polyuranate specimens were prepared by sintering of known amounts of triuranium octoxide with potassium carbonate or uranate, first at 600° and then at 800° [3]. In a number of cases, the composition of the uranates was checked

*Because of the lack of methods for obtaining single crystals of polyuranates of a higher degree of acidity than diuranates.

against the uranium content determined by the ammonia method. The deviations did not exceed the error in the analytical determination of the uranium content.

The results of phase analyses are given in Table 1. This table shows that in the $K_2O \cdot 3.1UO_3 - K_2O \cdot 6UO_3$ composition range the same phase is present; in view of its composition, we shall refer to it as potassium trihexauranate.

TABLE 2. Indexing of the $K_2O \cdot 3.4UO_3$ Powder Diagram

I	hkl	$\sin^2\theta_{meas} \cdot 10^4$	$\sin^2\theta_{calc} \cdot 10^4$	I	hkl	$\sin^2\theta_{meas} \cdot 10^4$	$\sin^2\theta_{calc} \cdot 10^4$
3	002	486	484	3	114	3456	3447
					210		3525
5	100	501	504	8	105	3539	3529
1,2	—	547	—				
10	101	629	625	8	211	3650	3646
				2	—	3802	—
1/2	—	750	—	4	204	3952	3950
1/2	—	850	—	4	212	4021	4009
1/2	—	937	—	1,2	—	4301	—
5	102	985	988	1	006	4370	4356
				2	300	4517	4532
					115		4536
1/4	—	1043	—	6	213	4651	4614
					301		4653
1	003	1088	1083	3	302	5024	5016
					205		5039
1,2	—	1198	—	1,2	—	5170	—
1/4	—	1352	—	4	214	5458	5461
1/4	—	1433	—	3	303	5624	5621
1/4	—	1471	—	4	116	5844	5867
8	110	1511	1510	3	220	6054	6043
8	103	1593	1584	3	221	6190	6164
8	111	1632	1632	1,2	206	6371	6370
1	—	1845	—	4	107	6428	6433
2	004	1926	1936	8	222	6538	6527
10	112	2008	1985		310		6547
	200		2014		215		6550
3	201	2136	1235				
1	—	2201	—	3	311	6653	6668
2	104	2253	2240	1	—	6773	—
8	202	2505	2498	1	—	6821	—
4	113	2607	2600	4	312	7026	7031
2	—	2731	—	4	223	7145	7132
3	203	3000	3003				

All the more or less strong lines of the trihexauranate can be indexed with the assumption of a hexagonal cell with $a \approx 4$ and $c \approx 7$ kX. The results of indexing of the powder diagram of the uranate $K_2O \cdot 3.4UO_3$ are given in Table 2. More precise values of the constants a and c for uranates of various compositions are given in Table 3. This cell is a subcell, and therefore a considerable number of weak lines cannot be indices (see Table 2).

It is clear from Table 2 that the fluctuations of line intensities are associated mainly with variations of the multiplicity factor. It is therefore reasonable to suppose that the uranium atoms, or at least the greater proportion of them, are situated at the sites of the subcell. In that case the shortest U – U distance (3.95-3.96 A) and the symmetry of the subcell indicate the presence of hexagonal uranyl–oxygen layers in trihexauranate. If a whole number of uranium atoms corresponds to the subcell, then the uranyl–oxygen layer must be defective (or layers of the composition UO_2O_2 and UO_2O must alternate [1]). If there are four oxygen atoms per cell and the composition of the layer is UO_2O_2, then some of the uranium atoms are not contained in the layer. Density measurements are in agreement with the latter variant:

	$\rho_{pycn.}$	$\rho_{calc.}$ with 1 uranium atom in cell	$\rho_{calc.}$ with 4 oxygen atoms in cell
$K_2O \cdot 3.1UO_3$	6.5	5.57	6.70
$K_2O \cdot 4.1UO_3$	6.6	5.38	6.64

Therefore, in the case of $K_2O \cdot 3.1UO_3$, one formula unit of the composition $K_{0.78}U_{1.2}O_4$ corresponds to the subcell. The layer composition is UO_2O_2 and, therefore, 0.78K and 0.2U per subcell are present between the uranyl–oxygen layers. Order in the arrangement of these atoms leads to the formation of a superstructure. In the general case the formula unit per cell has the composition $(K_2O \cdot nUO_3)_{4/3n+1}$. It is interesting to note that when the composition of trihexauranate alters not only the subcell, but probably also the true cell is retained; this is indicated by the fact that the positions of the superstructure lines remain unchanged (see Table 4).

TABLE 3. Parameters of the Trihexauranate Subcell (in kX)

$K_2O : UO_3$	a (±0.003)	c (±0.005)	$K_2O : UO_3$	a (±0.003)	c (±0.005)
1 : 2,9	3,955	6,993	1 : 4,1	3,960	6,992
1 : 3,1	3,952	6,980	1 : 5	3,959	6,986
1 : 3,4	3,958	6,996	1 : 6	3,961	6,987
1 : 3,6	3,956	6,989			

*Together with diuranate.

TABLE 4. Superstructure Lines in the X-ray Diagrams of $K_2O \cdot 3.4UO_3$ and $K_2O \cdot 5UO_3$

$K_2O \cdot 3.4UO_3$		$K_2O \cdot 5UO_3$		$K_2O \cdot 3.4UO_3$		$K_2O \cdot 5UO_3$	
I	$\sin^2\theta \cdot 10^4$	I	$\sin^2\theta \cdot 10^4$	I	$\sin^2\theta \cdot 10^4$	I	$\sin^2\theta \cdot 10^4$
1/4	547	1/2	539	1/2	1198	1/4	1214
1/2	750	1/2	746	1/4	1352	1/2	1367
1/2	850	1	852	1/4	1433	1/2	1436
1/2	937	1/2	932	1/4	1471	1/4	1478
1/4	1043	1/4	1027				

The arrangement of the potassium and uranium atoms situated between the layers can be determined only after the true unit cell has been found.

In a number of cases rhombic pseudohexagonal phases were formed in specimens with $UO_3/K_2O \approx 5.0$, as was shown by the observed splitting of lines in the powder diagrams. As an example, Table 5 shows the results of indexing of the powder diagram of $K_2O \cdot 5.65UO_3$ (a = 6.95 ± 0.02, b = 3.892 ± 0.005, c = 7.18 ± 0.02kX). This distortion may be caused either by a different arrangement of the atoms between the uranyl–oxygen layers or by the presence and ordering of oxygen defects in the layer. The formation conditions of the rhombic phases could not be determined to the end because the mutual transitions are extremely slow. However, it was found that they are formed if the uranate is synthesized at 600°; if the uranate is formed at 800° (after brief heating at 600°) the hexagonal phase is formed.

It is interesting to note the resemblance of precipitated potassium uranates to the trihexauranate. The x-ray patterns of two precipitated potassium uranates [4] are compared in Table 6 with the pattern of $K_2O \cdot 3.4UO_3$. The difference between the powder diagrams of the two hydrated uranates lies within the error limits of the measurement (the precision of which, or course, is less in this case because of the poorer quality of the patterns given by hydrated polyuranates). Both substances have the same parameters of the hexagonal cell (which is possibly a subcell): a = = 4.05 ± 0.01; c = 7.00 ± 0.03kX, i.e., they are fairly close to the parameters of anhydrous trihexauranates. The intensities also follow a generally similar course. It follows that precipitated potassium uranates contain uranyl–oxygen layers in which some of the oxygen atoms are replaced by hydroxyl groups. When the uranate is heated, removal of water is probably accompanied by some structural rearrangement and the uranyl–oxygen layer no longer contains water or hydroxyl ions. We found that the uranate $K_2O \cdot 4.1UO_3$ does not add on any appreciable amounts of water even when boiled for 6 hours.

TABLE 5. Indexing of the $K_2O \cdot 5.65UO_3$ Powder Diagram

I	hkl	$\sin^2\theta$ meas. $\cdot 10^4$	$\sin^2\theta$ calc. $\cdot 10^4$	I	hkl	$\sin^2\theta$ meas. $\cdot 10^4$	$\sin^2\theta$ calc. $\cdot 10^4$
1	001	114	115				
5	002	462	460	3	021	1676	1670
2	200	490	490	1/4	—	1694	—
5	110	512	514	3	004	1839	1840
5	201	609	605	1/4	—	1893	—
10	111	632	629	4	{312	1959	{1954
1/4	—	667	—		{400		{1960
1/4	—	745	—	4	022	2019	2024
1/2	—	805	—	1	{220	2053	{2054
					{401		{2075
1/2	—	835	—	4	224	2138	2169
1/2	—	855	—	3	{204	2330	{2330
2	202	971	950		{114		{2354
	112		974	2	402	2444	2429
1/2	—	995	—	8	{223	2506	{2512
					{313		{2519
1/4	003	1031	1035	3	023	2584	2589
1/2	—	1100	—	2	223	3095	3089
1/4	—	1173	—	4	{314	3356	{3354
					{205		{3365
1/2	—	1238	—	1	510	3458	3464
1/4	—	1294	—	3	{420	3525	{3524
					{511		{3560
1/2	—	1377	—	4	{421	3650	{3539
1	—	1472	—		{130		{3642
5	310	1516	1494	2	131	3762	3752
	203		1525				
2	113	1547	1549				
	020		1564				
3	311	1596	1599				

TABLE 6. X-ray Patterns of $K_2O \cdot 3.3UO_3 \cdot 4.1H_2O$; $K_2O \cdot 2.9UO_3 \cdot 3.0H_2O$ and $K_2O \cdot 3.4UO_3$

1 : 3.3 : 4.1		1 : 2.9 : 3.0				$K_2O \cdot 3.4UO_3$		
I	$\sin^2\theta$ meas. $\cdot 10^4$	I	hkl	$\sin^2\theta$ meas. $\cdot 10^4$	$\sin^2\theta$ calc. $\cdot 10^4$	I	hkl	$\sin^2\theta$ calc. $\cdot 10^4$
9	493	10	{002	490	{484	5	002	484
			{100		{481	5	100	504
10	605	10	101	611	602	10	101	625
4	970	3	102	967	965	4	102	988
2	1124	1	003	1097	1083	1	003	1083
5	1446	8	110	1463	1443	8	110	1510
8	1564	10	{103	1596	{1564	8	103	1593
			{111		{1564	8	111	1632
			{004		{1936	2	004	1936
6	1928	6	{112	1937	{1927	10	{112	{1995
			{200		{1924		{200	{2014
4	2058	6	201	2035	2045	3	201	2136
4	2206	3	—	2175	—	—	—	—
3	2393	4	{104	2412	{2417	2	104	2440
			{202		{2408	8	202	2498
3	2547	4	113	2547	2526	4	113	2600
2	3000	1	203	3017	3007	3	203	3103
3	3130	1	—	3124	—	—	—	—
3	3359	2	{214	3359	{3379	3	114	3447
			{210		{3367	8	{210	{3525
							{105	{3529
3	3475	2	{105	3460	{3506			
			{211		{3488	8	211	3646
			{115		{4468	2	115	4536
3	4448	2	{213	4452	{4456			
			{301		{4450	6	{213	{4614
							{301	{4653

Hydrated and anhydrous potassium uranates have some resemblance to sodium polyuranates [1] and to many minerals – hydrated uranates of barium and lead [5]. Either a hexagonal subcell with $a \approx 4$ and $c \approx 7$, or a rhombic (pseudohexagonal) cell corresponding to it can be identified in all these uranates. Our preliminary data on the structure of basic uranyl nitrates indicate the presence of pseudohexagonal $UO_2(OH, H_2O)_2$ layers in basic uranyl salts. In this connection, let us consider briefly the structure of uranate ions and multinucleate uranyl complexes in solution.

Various views on the arrangement of uranyl ions in the structure of water and experimental data on this problem have been considered by Lipilina [6]. The experimental results are in good agreement with an arrangement in which the uranyl ion is surrounded by six water molecules, which are arranged similarly to oxygen atoms in $CaUO_4$ and $Na_2U_2O_7$, oxygen and hydroxyl in hydrated polyuranates, hydroxyl in uranyl hydroxide (pseudohexagonal), and hydroxyl and water in basic uranyl salts. We therefore consider that it is reasonable to assume that multinucleate uranyl complexes are formed in solution by replacement of water molecules bound to uranyl by hydroxyl ions – in this case these multinucleate uranyl complexes are intermediate in structure and composition between uranyl ions in solution and sparingly soluble basic salts. Moreover, they are arranged in the structure of water without distorting it. During hydrolysis and titration with alkalies, water is first gradually replaced by hydroxyl ions (this is accompanied by formation, first, of complex ions, the solubility of which diminishes rapidly with increasing degree of polymerization, and then of insoluble basic salts). Subsequent phase transitions involve either a change in the composition of the $UO_2(O, OH, H_2O)_2$ layer, or an alteration in the mutual arrangement of the layers. All these processes may be schematically represented as follows:

$$\underset{\text{uranyl ion}}{UO_2(H_2O)_6^{2+}} \rightarrow \underset{\text{complex uranyl ion}}{(H_2O)_4UO_2(OH)_2UO_2(H_2O)_4^{2+}}$$

$$\underset{\substack{\text{uranyl–hydroxyl–}\\\text{hydrate layer in}\\\text{basic uranyl salts}}}{UO_2(OH, H_2O)_2^{n+}} \rightarrow \underset{\substack{\text{uranyl}\\\text{hydroxide}}}{UO_2(OH)_2} \rightarrow \underset{\substack{\text{layer in hydrated}\\\text{polyuranates}}}{UO_2(O, OH)_2^{n-}}$$

This scheme represents the variable composition of the phases formed, as the charge of the layer can vary continuously (this is indicated by the symbols +n and –n). The existence of extensive homogeneity regions has also been established for polyuranates [3, 7] and in part for basic uranyl nitrate.

According to Lipilina [6], multinucleate uranyl complexes have somewhat different structure which, in the case of the $U_2O_5^{2+}$ ion is represented by the formula $[(H_2O)_4UO_2OUO_2(H_2O)_4]^{2+}$, i.e., the uranyl ions are linked by oxygen and not by hydroxyl. It is difficult to agree with this because, first, the coordination number of uranium in neighboring representatives $UO_2(H_2O)_6^{2+}$ and basic salts is different (6), and, second, in compounds formed at higher pH values uranyl ions are linked only by hydroxyl ions (oxygen ions appear only in polyuranates). These views on the structure of $U_2O_5^{2+}$ and $U_3O_8^{2+}$ ions are associated with Lipilina's views [6] of the possible formation of two or three mutually perpendicular uranyl bonds. However, no such bonds have been demonstrated with sufficient certainty in the structures of uranyl compounds. If oxygen atoms form an octahedron around uranium it is, in fact, possible to identify three mutually perpendicular bonds, but these are nonequivalent (the length of the U – O bond in uranyl is appreciably less than the remaining U – O distances). The exception is cubic uranium trioxide (ReO_3 structural type), but a number of AX_3 compounds have a similar structure, i.e., in contrast to most structure of other compounds of U(VI), this structure is not specific for uranium. It is probable that, as in the structures of certain uranates with closest packing of large ions (such as potassium and oxygen), the uranyl group is not fixed in cubic UO_3.

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NORMAL AND DEFECT STRUCTURES OF THE PYROCHLORE TYPE

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 591-596, September-October, 1961
Original article submitted May 11, 1961

Possible fluctuations of the average valences of the cations in representatives of the $A_2B_2O_7$ – $A_2B_2O_6F$ series have been estimated on the basis of an analysis of the conditions for local compensation of valences in the pyrochlore structure. It was shown that the pyrochlore structural type is less characteristic for compounds of the $A_2B_2O_7$ type than for compounds of the $A_2B_2X_7$ type containing univalent cations.

In our previous investigation of pyrochlore [1] we utilized a polyhedral interpretation of its structure and attempted to explain some peculiarities of the structure and composition of pyrochlore and related minerals in terms of chemical crystallography. For example, it was suggested that there is a relationship between a deficiency of group A cations in comparison with the ideal A = 2 (in $A_2B_2X_7$) and defectiveness of the anionic portion of the structure. Results of further analysis of this group of compounds are presented in this paper.

The structure of pyrochlore (koppite) [3] is determined by a single parameter, and in the polyhedral concept it can be described as derived from the fluorite (CaF_2) structural type – cerianite (CeO_2), which is known to be characterized by three-dimensional checkerwork order in the distribution of the Ca(Ce) cubes. If we double the unit cell of the original structure along the edge and remove part of the F(O) anions, so that half the cubes lose two opposing vertices and become flattened octahedrons, we obtain the unit cell of the ideal pyrochlore structure, containing eight $A_2B_2X_7$ formula units. The operation described above results in doubling of the cubic-lattice constant and alters the symmetry of the structure (space group $Fd\bar{3}m$ instead of $Fm\bar{3}m$). In the resultant model each X anion is the meeting point of four polyhedrons*: two cubes and two octahedrons meet on each of 48 X atoms of the pyrochlore cell which are on twofold axes, and four cubes meet at each of the remaining eight (situated in a position without parameters – special points of $\bar{4}3m$ symmetry). Analysis showed that because of the high symmetry in real structures of the pyrochlore type, deviation of the parameter $\underline{x}$ of the 48-fold complex of x00 oxygen atoms from the ideal value x = 0.25 cannot lead to a change in the coordination numbers of the cations. All that is possible is distortion of the cubes of the ideal model and changes in the form of the flattened octahedrons of the latter.

A characteristic feature of minerals of the pyrochlore group (pyrochlore, microlite, betafite, etc.) is the complexity and inconstancy of their chemical composition. Thus, the general formula of the minerals of this $A_2B_2X_7$ group can be written in the following expanded form: $(Ca, Na, TR, U)_2(Nb, Ta, Ti, Fe)_2O_6(F, OH, O)$, the cubes of the structure being filled with cations A (Ca, etc.), and the octahedrons with cations B (Nb, etc.). Another characteristic feature of this group is the frequently observed metamict state, especially in the case of specimens containing considerable amounts of rare earths U and Ti. Nonmetamict specimens are usually simpler in composition and correspond to the formula $(Ca, Na)_2(Nb, Ta)_2O_6(F, OH, O)$. The possibility of extensive isomorphic substitution in the pyrochlore structure which follows from the foregoing formulas is quite reasonable, because groups A and B include cations of relatively similar size, for which coordination numbers of eight and six, respectively, are natural. However, it can be shown that a purely geometrical treatment of the structure is insufficient for explaining certain very significant features of representatives of the pyrochlore structural type. We therefore supplemented the spatial characteristics by considerations which follow from the necessity of local compensation of valences in the structure, as is formulated in Pauling's well-known second rule. Repeated verification of this rule with known crystal structures revealed that in the great majority of cases the deviation of the sum of the positive valence forces converging

*But not a junction of two cubes and two octahedrons for all anions, as was stated through a misunderstanding in [1].

on each anion of the structure does not exceed 25% of the valence of the anion. Therefore the value given can be confidently regarded as being close to the limiting value, since in reality many structures are characterized by deviations considerably smaller than 25%.

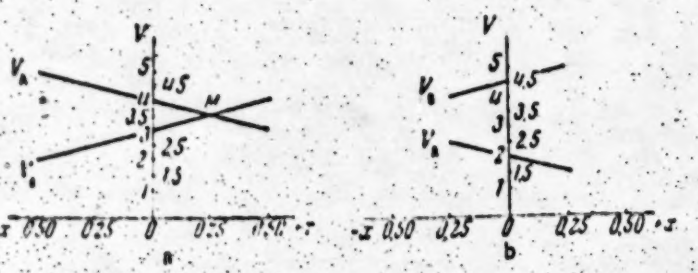

Fig. 1. Variation of the average valences of cations with x for compounds $A_2B_2O_7$ (a) and $A_2B_2O_6F$ (b).

A structure in which the deviation of the sum of positive forces at each anion does not exceed 25% of its valence we shall describe as "energetically stable." In relation to the pyrochlore structure, the next starting point for subsequent reasoning is the fully justified assumption that the univalent anions (F,OH) in the structure are situated at the 48m points of symmetry of the nonparametric regular system (meeting points of four cubes). If the seventh anion in the pyrochlore formula is represented simultaneously by F, OH, and O, we assume that anions of this kind are distributed statistically at the points of the above-named eightfold position. Finally, we shall start with a nondefective structure, i.e., we assume that the structure corresponds ideally to the formula $A_2B_2X_7$.

We write the formula of pyrochlore as $A_2B_2O_6(F,O)$ and assume that all members of the series $A_2B_2O_7$ – $A_2B_2O_6F$, which are regarded as stable in the sense indicated above, can exist.

We now introduce the following notation:

p is the valence of the hypothetical ion (F,O), $1 \leq p \leq 2$; x is the deviation of the sum of local valence forces from p, $0 \leq |x| \leq 0.25p$; V_A is the average valence of the cations in the cubes; V_B is the average valence of the cations in the octahedrons.

$4V_A/8$ positive forces converge on anions of valence p, and therefore we can write $V_A/2 = p - x$. Taking into account that the number of "normal" oxygen atoms in the structure is six times the number of "hypothetical" (F,O) ions, and also satisfying the condition that the sum of the deviations of the valence forces must be zero, we now write the following equation: $2V_A/8 + 2V_B/6 = 2 + x/6$. Substituting the expression for V_A into this equation we obtain the formulas connecting the average cation valences with x: $V_A = 2p - 2x$ and $V_B = (6 - 3p/2) + 2x$.

For the end members of the series of compounds in question we therefore have:

$$A_2B_2O_7\ (p = 2) \qquad\qquad A_2B_2O_6F\ (p = 1)$$

$$\left.\begin{aligned} V_A &= 4 - 2x \\ V_B &= 3 + 2x \end{aligned}\right\} |x| \leq 0.50 \qquad \left.\begin{aligned} V_A &= 2 - 2x \\ V_B &= 9/2 + 2x \end{aligned}\right\} |x| \leq 0.25$$

The relationships corresponding to these equations are plotted in Fig. 1a, b; they consist of intercepts of straight lines in the corresponding ranges of x. From the graph for $A_2B_2O_7$ (Fig. 1a) we have the following valence fluctuations possible for a stable structure: $V_A = 3.0 - 5.0$ and $V_B = 2.0 - 4.0$. In the range of $-0.5 \leq x < +0.25$ the average valence of cations in the octahedrons must be less than the valence of cations in the cubes and only to the right of point M do we have $V_B > V_A$. In order to apply these results to real structures, we must take into account the geometrical characteristics of the atoms; namely, their dimensions. Thus, for the great majority of pairs of different cations the larger cation has lower valence, and vice versa. Therefore, the condition $V_A > V_B$ over the entire range to the left of point M (Fig. 1a) can in reality be satisfied only in the rare cases where the group A cations are simultaneously large and have high valence (for example, in the compound $Th_2Fe_2O_7$). The required condition $V_B > V_A$ to the right of point M is satisfied over only a small range of x.

Turning to Fig. 1b, we note that for compounds of the type $A_2B_2O_6F$ the average valences V_A and V_B for all possible values of x are consistent with the sizes of the corresponding cations of low and high valences.

These graphs can also be used for estimating V_A and V_B for intermediate members of the series in question. Figure 2a shows the same, but differently arranged, plots of the average valence of cations in cubes against x for the two end members of the series, and Fig. 2b shows the corresponding graphs for the cation valences in octahedrons (continuous lines). Joining the ends of the lines (by broken lines) we obtain regions in the form of trapeziums. Knowing the value of p for a given intermediate member of the series, and drawing a straight line through a certain point (determined by the value of p) on the ordinate axis parallel to the bases of the trapezium until it cuts the sides, we obtain a graph for the given compound, similar to the graphs for the two extreme cases. By projection of the ends of the resultant intercept onto the ordinate axis we can estimate fluctuations of V_A and V_B possible within the established stability limits for a given compound.

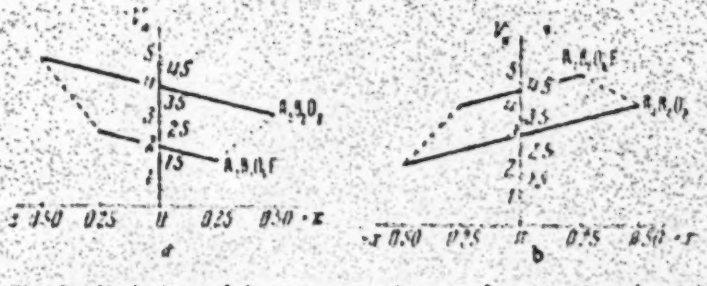

Fig. 2. Variations of the average valences of cations in cubes (a) and octahedrons (b) with x.

It follows from the foregoing that the pyrochlore structural type is less characteristic (or less probable) for compounds of the $A_2B_2O_7$ type than for compounds of the $A_2B_2O_6F$ type. This accounts for the very great rarity of natural compounds crystallizing in the pyrochlore structural type and strictly corresponding to the composition $A_2B_2O_7$. On the other hand, the stability of structures of the $A_2B_2O_6F$ type is confirmed by the very frequent natural occurrence of nonmetamict minerals of the pyrochlore group, the seventh anion in the formulas of which is represented almost entirely by F^- or OH^-. These ions bring into line the energetic and geometrical conditions for stability of the pyrochlore structural type.

So far we have assumed that the compound under investigation corresponds ideally to the formula $A_2B_2X_7$. Let us now suppose that there exists a structure of the pyrochlore type defective in the anionic portion; for example, corresponding to the formula $A_2B_2O_6O_{0.5}$. On the basis of our main postulate, this structure may be regarded as stable if it is assumed that four oxygen atoms in the pyrochlore cell, corresponding to the seventh anion of the ideal formula, are distributed statistically between the points of the eightfold position. In this case, the average valence p of the seventh anion in the formula is unity and we therefore have the variant $A_2B_2O_6F$, which has already been considered. Therefore, it may be concluded that in order to retain energetic stability, compounds not containing univalent anions should exhibit a tendency to form structure defective in the anionic portion. A consequence of this defectiveness, according to [1], may be a deficiency of group A cations.

Very weighty direct evidence of the frequent defectiveness of the real structures of the minerals in question is provided by the results calculated from chemical analyses; these usually lead to nonstoichiometric formulas of the type $A_{2-y}B_2O_6(F, OH, O)_{1-z}$. In the light of the foregoing, this formula is quite reasonable and should not cause perplexity. In this connection we may refer to a recent mineralogical paper [4], the authors of which correctly accept the idea that the anionic portion of the pyrochlore structure is frequently defective; however, the categorical denial of the possibility of hydroxyl groups entering the pyrochlore structure surprised us. If we assume, in accordance with the reasoning in the present paper, that univalent anions increase the stability of the pyrochlore structural type, there can be no obstacles to OH^- groups entering the structure together with F^- ions. Therefore, despite the fact that the conclusions in the paper cited are based on experimental investigations by the methods of infrared spectroscopy, the results and their interpretation require thorough verification with a large number of specimens.

Let us now consider artificial compounds of the $A_2B_2O_7$ type, and in particular $A_2^{2+}Ti_2O_7$ and $A_2^{2+}Nb_2O_7$. Some of them are ferroelectric materials, which accounts for the great interest in synthesis and investigation of such compounds. It is stated in [5] that with the exception of $La_2Ti_2O_7$ and $Nd_2Ti_2O_7$, rare-earth tantalates with large RE^{3+} ions (and also Y^{3+}) crystallize in the pyrochlore structural type. Turning to Fig. 1a we note that when $V_A = 3$ and

$V_B = 4$, the value of $x = 0.5$ and, therefore, the compounds $A_2^{2+}Ti_2O_7$ represent the stability boundary of the pyrochlore structural type. It is impossible to establish the exact stability boundary and, therefore, we can only say that the crystalline structures in question are near the boundary of their stability. Since the value of x in these structures does not exceed 25% of the valence of oxygen atoms, the crystal structures of these compounds need not yet exhibit anionic defectiveness. It also follows from our graphs that the compounds $A_2^{2+}Nb_2O_7$ lie far beyond the stability boundary established for the pyrochlore structural type. We therefore conclude that the pyrochlore structural type is improbable for these compounds, and if it does occur the compounds should exhibit a tendency to form defect structures. In fact, most compounds of the type $A_2^{2+}Nb_2O_7$ (and $A_2^{2+}Ta_2O_7$) do not crystallize in the pyrochlore type and have symmetry lower than cubic [6]. It is interesting to note that one representative of this group, $Pb_2Nb_2O_7$, has rhombohedral symmetry, whereas the $Pb_{1.5}Nb_2O_{6.5}$ defect structure has true cubic symmetry [7]. Evidently both the geometrical and the energetic conditions favoring the formation of pyrochlore structure improve sharply as we pass from $Pb_2Nb_2O_7$ to $Pb_{1.5}Nb_2O_{6.5}$. Indeed, the Pb^{2+} ion, which is too large for eightfold coordination (radius 1.26 A) is replaced in the second compound by a "hypothetical" ion of radius $1.26 \cdot \frac{3}{4} = 0.95$ A, as 12 atoms in the $Pb_{1.5}Nb_2O_{6.5}$ cell are distributed statistically among the points of the sixteenfold position. The radius 0.95 A is close to the optimum value necessary for group A cations, and therefore the geometrical conditions are well satisfied for the compound $Pb_{1.5}Nb_2O_{6.5}$. Our quantity p has the value of 1 for the defect structure in question. It follows from Fig. 1b that when $V_A = 1.5$ and $V_B = 5.0$, $x = 0.25$, i.e., we have the maximum value of x, but one which is still permissible for a stable structure.

An example of the few compounds which do not conform to our conclusions is $Cd_2Nb_2O_7$. Complete x-ray structural investigation of $Cd_2Nb_2O_7$ single crystals showed that it belongs to the pyrochlore structural type [8]. Whereas in other similar cases there may be doubts whether the stoichiometric proportions 2:2:7 are maintained, this Cd niobate conforms satisfactorily to these proportions. Although complete chemical analysis of these crystals was not carried out, evidence for this is provided by the very favorable value of the divergence factor $R = 0.06$, found from the ideal proportions $A:B:O = 2:2:7$. Thus, on each of eight oxygen atoms in the $Cd_2Nb_2O_7$ cell there is only one positive valence which, as has been noted, is a very rare case (x is double the limiting 25%). In the author's opinion, the existence of a small number of structures similar to $Cd_2Nb_2O_7$ does not refute the main conclusions of this investigation, as we are concerned here not with categorical possibility or impossibility of the pyrochlore structural type, but merely with general tendencies, in accordance with the tentative nature of the original postulates.

In conclusion, it must be pointed out that in a number of cases it may be very difficult to establish the presence of the pyrochlore structural type from x-ray diffraction data. For example, with similar scattering power of atoms of groups A and B, the reflections from h, k, and $l = 2n + 1$ are very weak and may not appear in the patterns; in that case the patterns are indexed on the basis of a cell with its edge halved. Therefore, despite the presence of a fully ordered structure of the pyrochlore type, it is possible to draw the erroneous conclusion that A and B cations in a cell of the CeO_2 type are present in a disordered arrangement. For example, such an error may occur in the case of the compound $Cd_{2-y}Nb_2O_{7-y}$, if y is small. A case is also possible when the sharp diffraction picture in the powder diagram, characteristic of ordered pyrochlore, is complicated by a certain number of weak nonindexable reflections; the latter may not be recorded on the pattern at all, or they may be attributed to the presence of more than one phase in the specimen. It may be the case in reality that we are concerned with a single crystalline phase which is not of the pyrochlore structural type, but is another derivative of the basic $CaF_2 - CeO_2$ structure. An example is the recently interpreted structure of the mineral calciotitite [9].

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RESOLUTION OF π-ELECTRON ENERGY OF AROMATIC CONDENSED MOLECULES BY BONDS BY DIFFERENT VARIANTS OF THE SIMPLEST MO LCAO METHOD

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 597-603, September-October, 1961
Original article submitted June 4, 1960

It is shown for two variants of the simplest MO LCAO method: 1) introduction of resonance integrals β_{ij} differing in magnitude in accordance with the bond type (with $\beta_{ij} \neq 0$ only for neighboring atoms), and 2) introduction of overlap integrals in the same approximation, that the π-energy of aromatic condensed systems can be represented with sufficient accuracy in the form of a linear function (with coefficients independent of the particular molecule) of the numbers of definite bond types characteristic of the given series of molecules; i.e., this energy is additive for the bonds.

Calculation of hydrocarbon energies by different variants of the MO method is at present an extremely laborious task, virtually impossible for hydrocarbons with large numbers of atoms. Moreover, purely theoretical calculations do not give numerical results of the desired precision. It is more important from the practical aspect to establish the general qualitative relationships which follow from different variants of the MO method and, in the first instance, to solve the problem of the relation of the properties being calculated to the structure of the molecules. For example, in the phenomenological theory of the relation between properties and structure the following postulate, confirmed by very numerous experimental data, has long been adopted: the energy of any representative of a given molecular series can be represented as the sum of partial quantities corresponding to individual local structural elements of the molecules, the properties of which are regarded as unchanged in all the molecules of the given series. It follows that any theory which is claimed to reflect experimental relationships must lead to the same relation between energy and structure. Here a very interesting question from the theoretical aspect is how this relation follows from the structure of the calculation methods themselves, from the methods for determining the wave functions of the molecules.

This question was examined for a number of condensed aromatic systems by the simplest variant of the MO LCAO method – Hückel's variant [1]. It was shown that the π-electron energy of these hydrocarbons can be represented with sufficient accuracy [2] in the form of a linear function of the numbers of definite bond types characteristic of the given molecular series; it was thereby established that the above postulate of the phenomenological theory is valid within the framework of this variant of the MO LCAO method.

In the present communication we consider the validity of this postulate in more complex variants of the MO LCAO method, in which differences between the magnitudes of the resonance integrals are taken into account and overlap integrals are introduced.

1. Introduction of Overlap Integrals in the Hückel Variant of the MO LCAO Method

In the simplest variant of the MO LCAO method, considered in [1], the following are assumed equal: 1) the Coulomb integrals $\alpha_{ii} = \alpha$, and 2) the resonance integrals $\beta_{ij} = \beta$ for neighboring atoms. The remaining integrals, for nonadjacent atoms, are assumed to be zero. The integrals $S_{ij} = \int \varphi_i^* \varphi_j d\tau$ are assumed equal to δ_{ij}. As has been pointed out by several authors [3,4], disregard of the overlap integrals S_{ij} ($i \neq j$) has a significant influence on the calculation results.

Let us suppose that S_{ij} are different from zero for neighboring atoms and are all equal to each other. This assumption is more accurate when Slater atomic orbitals are used, than the assumption that the resonance integrals

are equal to each other [5]. Therefore, as soon as we accept the last assumption ($\beta_{ij} = \beta$), it is reasonable to take all the overlap integrals as equal ($S_{ij} = S$). For the $2p_\pi$ Slater orbitals, the value of 0.25 is usually chosen for S (with R = 1.39 A and $Z_{eff} = 3.18$, S = 0.25889).

The matrix elements $H - \epsilon S$ of the secular equation

$$(H - \varepsilon S)\, c = 0 \tag{1}$$

are of the form $\alpha - \epsilon$ if $i = j$; $\beta - \epsilon S$, if $i \neq j$ (i and j are neighboring atoms), and 0 in all other cases. We divide the matrix $H - \epsilon S$ by the scalar $\beta - \epsilon S$. Equation (1) becomes

$$\left(A - \frac{\varepsilon - \alpha}{\beta - S\varepsilon} E\right) c = 0, \tag{2}$$

where A is the matrix of the Hückel variant of the MO method with the elements: $a_{ij} = 1$ if i and j are neighbor-atoms, and $a_{ij} = 0$ in all other cases (including $i = j$). We denote $\frac{\epsilon - \alpha}{\beta - S\epsilon}$ by x. Then Eq. (2) formally coincides with the equation

$$(A - xE)\, c = 0 \tag{3}$$

of the usual Hückel variant without the overlap integrals. The eigenvalues of Eq. (1) can be found from the eigenvalues of Eq. (3) with the aid of the equation

$$\varepsilon = \frac{\alpha + \beta x}{1 + Sx}$$

or by introducing the new quantity $\gamma = \beta - S\alpha$,

$$\varepsilon = \alpha + \frac{\gamma x}{1 + S\varepsilon}. \tag{4}$$

By viture of the symmetrical arrangement of the eigenvalues of matrix A, we can write the following expression for the π-electron energy:

$$W_\pi = 2 \sum_{i=1}^{N/2}{}' \varepsilon_i = N\alpha + 2\gamma \sum_{i=1}^{N/2}{}' \frac{x_i}{1 + Sx_i} \tag{5}$$

or

$$W_\pi = N\alpha + \gamma \sum_{i=1}^{N}{}' \frac{|x_i|}{1 + S|x_i|}. \tag{6}$$

Therefore, to determine W_π we must find $\sum_{i=1}^{N}{}' \frac{|x_i|}{1 + S|x_i|}$ or, taking into account that $|x_i|$ are the eigenvalues of matrix $|A|$, the value of $Sp[|A| \cdot (E + S|A|)^{-1}]$. The fraction $\frac{|x_i|}{1 + S|x_i|}$ can be found approximately by representing it as a series in powers of x_i or series of x_i polynomials, and then terminating these series to obtain the final expressions.

Since $|x_i| \leq 3$, expansion into Taylor series is possible when S = 0.25. However, the series converges rather slowly. It is therefore more convenient to use the following procedure: write for the function $f(x) = |x|(1 + S|x|)$ an approximate expression in the form of the polynomial $P_n(x) = a_0 + a_1 x + a_2 x^2 + \ldots + a_n x^n$, and then find the best values of the coefficient by one method or another. In particular, the coefficients a_i can be found from the minimum of the root mean square deviation of the polynomial $P_n(x)$ from the function $f(x)$ over the given range of $f(x)$. Here it should be noted that since $f(x)$ is an even function, all the a_i coefficients with odd i are equal to zero. Taking the tenth-order polynomial P_{10}, we have

$$P_{10} = 0{,}165136 + 0{,}984098\, x^2 - 0{,}421968\, x^4 + 0{,}0971609\, x^6 - 0{,}0105171\, x^8 + 0{,}000425144\, x^{10}. \tag{7}$$

The traces of powers of matrix A can be represented as linear functions of the numbers of definite configurations or bond types [1,6] in the given molecular series. Using this concept, we finally have* for W_π:

*Here and in subsequent similar expressions, α is taken as zero and W_π is given in γ units.

$$W_\pi = 0{,}97999\, m_{22}^1 + 0{,}97772\, m_{22}^2 + 0{,}98394\, m_{22}^3 + 0{,}82202\, m_{23}^1 + \\ + 0{,}82212\, m_{23}^2 + 0{,}81594\, m_{23}^3 + 0{,}82029\, m_{33}^1 + 0{,}71332\, m_{33}^2 + \\ + 0{,}70875\, m_{33}^3 + 0{,}70445\, m_{33}^4 + 0{,}71269\, (m_{33}^{4\,\mathrm{int}})_{\mathrm{cis}} + 0{,}70844\, (m_{33}^{4\,\mathrm{int}})_{\mathrm{trans}} + \\ + 0{,}71367\, m_{33}^{4\,\mathrm{ext}} + 0{,}71263\, m_{33}^{5\,\mathrm{int}} + 0{,}70559\, m_{33}^{5\,\mathrm{ext}} + 0{,}72108\, m_{33}^{6\,\mathrm{int}} + 0{,}70175\, m_{33}^{6\,\mathrm{ext}}. \tag{8}$$

[The symbols used for bond types are given in [2]. In Eq. (8), as in all the subsequent expressions of the energy as a linear function of the numbers of bond types, it might be possible, for the sake of generality, to introduce the coefficients c_1, c_2, c_3, and c_4 to take into account the linear relationships between m_{ij}^f, as was done in [2]. However, in order to simplify matters, we do not do this.]

For approximation $f(x)$ we can use a polynomial of somewhat different form, from which there follows directly the connection between the expression for W_π when $S \neq 0$ and the expression for $W_\pi^{(0)}$ when $S = 0$:

$$\frac{|x|}{1 + S|x|} = a_1|x| + a_0 + a_2x^2 + a_4x^4 + \ldots + a_{2n}x^{2n}, \tag{9}$$

which, with $S = 0.25$, leads to:

$$W_\pi = 0{,}98475\, W^{(0)} - 0{,}33506\, m_{22}^1 - 0{,}33456\, m_{22}^2 - 0{,}33420\, m_{22}^3 - \\ - 0{,}32216\, m_{23}^1 - 0{,}32179\, m_{23}^2 - 0{,}32149\, m_{23}^3 - 0{,}32120\, m_{23}^4 - \\ - 0{,}31462\, m_{33}^1 - 0{,}31403\, m_{33}^2 - 0{,}31343\, m_{33}^3 - 0{,}31357\, (m_{33}^{4\,\mathrm{int}})_{\mathrm{cis}} - \\ - 0{,}31350\, (m_{33}^{4\,\mathrm{int}})_{\mathrm{trans}} - 0{,}31282\, m_{33}^{4\,\mathrm{ext}} - 0{,}31304\, m_{33}^{5\,\mathrm{int}} - 0{,}31222\, m_{33}^{5\,\mathrm{ext}} - \\ - 0{,}31265\, m_{33}^{6\,\mathrm{int}} - 0{,}31170\, m_{33}^{6\,\mathrm{ext}}. \tag{10}$$

Here $W_\pi^{(0)}$ is the value of the π-electron energy calculated for $S = 0$. If we take the expression from [2] for $W^{(0)}$, we obtain a formula for W_π which virtually coincides with Eq. (8). In calculations with Eq. (10) the value of $W_\pi^{(0)}$ may be taken either from precise calculations or from approximate formulas (for example, from [2,7]).

It can be shown that the absolute magnitude of the error in calculation of W_π from Eq. (8) differs only slightly from the absolute magnitude of the error in calculation of $W_\pi^{(0)}$; i.e., the error does not exceed 1%. The same conclusion can be reached by a direct comparison of the calculated values with the available exact values [8,9]. The error in calculation by Eq. (10) with the use of exact values of $W_\pi^{(0)}$ is considerably less (not over 0.1% and, in the great majority of cases, of the order of 0.01%).

2. Introduction of Different β_{ij} for Different Bonds

A question of no less interest is how the structure of the expression for the energy W_π is influenced by introduction of the difference between the integrals β_{ij} for different bonds (assuming again that β_{ij} are different from zero only for directly linked atoms). Such differences were introduced, for example, by Ruedenberg [10], in comparison with the Hückel variant of the MO method with the free-electron method.

In this case, the matrix elements $H - \epsilon S$ are: $\alpha - \epsilon$ if $i = j$; $\beta_{ij} - \epsilon S_{ij} = \gamma_{ij} - (\epsilon - \alpha)S_{ij}$, if $i \neq j$; and 0 in all other cases (here i and j are neighboring atoms; $\gamma_{ij} = \beta_{ij} - \alpha S_{ij}$). We assume further that $\gamma_{ij} = b_{ij}\gamma$, $S_{ij} = b_{ij}S$, i.e., that γ_{ij} and S_{ij} are proportional to each other. As was shown by the calculations of van Dranen [5], this is a somewhat crude approximation (if $-\gamma_{ij} = 1.9$-2.8 ev, this proportionality holds in the range of ± 0.25 ev), but it is considerably better than the approximation $S_{ij} = 0$ ($i \neq j$). Dividing the matrix $H - \epsilon S$ by the scalar $\gamma - (\epsilon - \alpha)S$ and denoting $(\alpha - \epsilon)/\gamma - (\epsilon - \alpha)S$ by $-x$, we have the secular equation in the form

$$(B - xE)c = 0, \tag{11}$$

where the elements of matrix B are equal to b_{ij} if i and j are neighboring atoms, and 0 in all other cases. Since $\epsilon_i = \alpha + \gamma\frac{x_i}{1 + Sx_i}$ and matrix B has the same symmetrical arrangement of roots as matrix A, we have

$$W_\pi = 2\sum_{i=1}^{N/2} \epsilon_i = 2\sum_{i=1}^{N/2} \alpha + 2\gamma \sum_{i=1}^{N/2} \frac{x_i}{1 + Sx_i} = \\ = \alpha N + \gamma \sum_{i=1}^{N} \frac{|x_i|}{1 + S|x_i|} = \alpha N + \gamma Sp\,[|B|(E + S|B|)^{-1}]. \tag{12}$$

The matrix $|B|(E + S|B|)^{-1}$ can be represented as a series of powers of matrix B (over the range of existence of eigenvalues of the latter), or approximately in the form of a polynomial based on matrix B with coefficients determined by one method or another (see Section 1).

We write the following approximate formula for $|B|(E + S|B|)^{-1}$:

$$|B|(E + S|B|)^{-1} = a_0E + a_1|B| + a_2B^2 + a_4B^4 + \ldots + a_{2n}B^{2n}. \quad (13)$$

then

$$W_n = \alpha V + a_0\gamma_i V + a_1\gamma_i Sp|B| + \gamma_i Sp(a_2B^2 + a_4B^4 + \ldots + a_{2n}B^{2n}). \quad (14)$$

The traces of matrices $B^2, B^4, \ldots$ like the traces of matrices A^{2n}, can be expressed as linear functions of the number of definite types of bond configurations or of definite bond types in the given molecular series. However, these expressions are much more complex for matrix B^{2n} than for matrix A^{2n}. It is therefore more convenient to represent matrix $|B|(E + S|B|)^{-1}$ by the polynomial (13) and not by the polynomial $P_{2n}(B) = a_0E + a_2B^2 + a_4B^4 + \ldots + a_{2n}B^{2n}$, as in the former case a polynomial of lower order can be taken for obtaining the same precision as in the latter.

The matrix trace $|B|$ is determined with the aid of the perturbation theory. The elements of matrix B, equal to b_{ij} for neighboring atoms, differ little for different bonds in hydrocarbons and are fairly close to 1. Thus, according to [5], the expression $0.80 \leq b_{ij} \leq 1.14$ is valid for benzene, naphthalene, and anthracene with $\gamma = -2.42$ ev. In [10], for determination of agreement with the free-electron method, it was assumed that $\gamma_{ij} = T_iT_j\gamma$, where $T_i = 1$ if $\underline{i}$ is a nonjoint C_2 atom, and $T_i = (^2/_3)^{\frac{1}{2}}$ if $\underline{i}$ is a joint C_3 atom. The author points out that this large difference between the values of γ_{ij} probably does not correspond to reality.

In the light of the foregoing, we can take a matrix in which all the b_{ij} ($i \neq j$, $\underline{i}$ and $\underline{j}$ are neighboring atoms) are equal to each other ($= b$) as the unperturbed matrix for B.

Then

$$B = b\Lambda + V, \quad (15)$$

where V is the perturbing matrix with the elements $v_{ij} = b_{ij} - b$, if $\underline{i}$ and $\underline{j}$ are neighboring atoms, and $v_{ij} = 0$ in all other cases. We assume that v_{ij} are small, so that the series of the perturbation theory converges for all the eigenvalues. Moreover, we assume that we can, with a sufficient degree of accuracy, confine ourselves to the theory of first-order perturbations.

Therefore,

$$W_n = bW_n^{(0)} + \sum_{n=1}^{N/2} g_nV_{nn}, \quad (16)$$

where $V_{nn} = c_n^+Vc_n$, $W_\pi^{(0)}$ is the π-electron energy calculated from the secular equation (3), and $g_n = 0$, 1, or 2 is the number of electrons at the $\underline{n}$ level. In this instance $g_n = 2$ for $n = 1, 2, \ldots N/2$, and $g_n = 0$ for $n = (N/2) + 1, \ldots$ (N is the order of matrix A).

Let us consider the term $\sum_{n=1}^{N/2} V_{nn}$. In expanded form it may be written:

$$\sum_{n=1}^{N/2} V_{nn} = \sum_{n=1}^{N/2}\sum_{i,j=1}^{N} c_{ni}^*c_{nj}v_{ij}. \quad (17)$$

By definition $2\sum_{n=1}^{N/2} c_{ni}^*c_{nj} = p_{ij}$, where p_{ij} is the order of the $i - j$ bond. Therefore,

$$2\sum_{n=1}^{N/2} V_{nn} = \sum_{i,j=1}^{N} p_{ij}v_{ij} = 2\sum_{i<j}^{N} p_{ij}v_{ij}. \quad (18)$$

The bond orders can be found approximately by differentiation with respect to β_{ij} of the power series of matrix A used for determination of $W_\pi^{(0)}$, or obtained by direct calculation for particular hydrocarbons. Both methods lead to the conclusion that these orders are constant, to within ±10% for each bond type. Since the term $\sum_{i,j=1} p_{ij}v_{ij} \ll bW_n^{(0)}$,

it is to be expected that the error in determination of W_π would be considerably less than 10%. Comparison of the values of W_π calculated by this method with the accurate values shows that this is so. Moreover, it can also be assumed with the same degree of approximation that v_{ij} are also constant for each bond type.

Thus, if p_{ij} and v_{ij} are assumed constant for each bond type, we have

$$W_\pi = bW_\pi^{(0)} + \sum_{(i,j,l)}{}' p_{ij}^l v_{ij}^l m_{ij}^l, \tag{19}$$

where p_{ij}^l is the order of the bond of the $\{i, j, l\}-$th type, v_{ij}^l is a certain constant quantity characteristic for a bond of a given type, and m_{ij}^l is the number of such bonds. Since, as has been shown earlier [1], $W_\pi^{(0)}$ can be represented as the sum for the different bonds, we again have a representation of the energy W_π in the form of a linear function of the number of certain bond types, characteristic of the given molecular series, with coefficients which are independent of the actual type of molecule in the given series.

Let us consider the case $S = 0$. For numerical calculations we use the bond orders calculated by Ham and Ruedenberg [11] and Hall [12] for 33 hydrocarbons. The average bond orders then have the following values (the symbols for bond-orders are the same as for the numbers of bond types; these symbols are given in detail in [2]):

$$\begin{array}{llll} p_{22}^1 = 0{,}6149 & p_{23}^3 = 0{,}5968 & p_{33}^3 = 0{,}5205 & p_{33}^{s\,int} = 0{,}5449 \\ p_{22}^2 = 0{,}7019 & p_{23}^4 = 0{,}6400 & (p_{33}^{s\,int})_{cis} = 0{,}5547 & p_{33}^{s\,ext} = 0{,}4817 \\ p_{22}^3 = 0{,}7619 & p_{31}^1 = 0{,}4806 & (p_{33}^{s\,int})_{trans} = 0{,}5460 & p_{33}^{s\,int} = 0{,}5278 \\ p_{23}^1 = 0{,}5340 & p_{33}^2 = 0{,}5206 & p_{33}^{s\,ext} = 0{,}4533 & p_{33}^{s\,ext} = 0{,}5134 \\ p_{23}^2 = 0{,}5813. & & & \end{array}$$

As an example we take the so-called F-variant of the MO method [10], when the matrix B is determined by the conditions: $b_{ij} = T_i T_j b$, when $i \neq j$ (i and j are neighboring atoms) and b_{ij} in all other cases; $T_i = 1$ if i is a nonjoint C_2 atom, and $(2/3)^{\frac{1}{2}}$ if i is a joint C_3 atom. Using the bond orders given above and the formula for $W_\pi^{(0)}$ from [2], we can obtain expressions for W_π which differ little from each other in accordance with the selection of $b(^2/_3 \leq b \leq 1)$. In particular, when $b = {}^5/_6$ we have:

$$\begin{aligned} W_\pi = {} & 1{,}3173\, m_{22}^1 + 1{,}3252\, m_{22}^2 + 1{,}3309\, m_{22}^3 + 0{,}9525\, m_{23}^1 + 0{,}9366\, m_{23}^2 + \\ & + 0{,}9254\, m_{23}^3 + 0{,}9134\, m_{23}^4 + 0{,}7780\, m_{33}^1 + 0{,}7433\, m_{33}^2 + 0{,}7220\, m_{33}^3 + \\ & + 0{,}7180\, (m_{33}^{s\,int})_{cis} + 0{,}7172\, (m_{33}^{s\,int})_{trans} + 0{,}7455\, m_{33}^{s\,ext} + 0{,}7035 m_{33}^{s\,int} + \\ & + 0{,}7147\, m_{33}^{s\,ext} + 0{,}6988\, m_{33}^{s\,int} + 0{,}6855\, m_{33}^{s\,ext}. \end{aligned} \tag{20}$$

Comparison of the values of W_π calculated from this formula with the available exact values [13] shows that the deviations, except in the case of benzene, do not exceed 0.3%; for benzene the error is 1.2%.

We now consider the case when $S \neq 0$. It is evident that the linear dependence on the numbers of definite bond types (or bond configurations) with coefficients constant for all the molecules of a given series holds in this case also. The maximum order of polynomial (13) needed to give the required precision depends on the limits within which lie the eigenvalues of matrix B, and on the value of S. As an example, let us consider the same F-variant of the MO method with introduction of the overlap integral $S = 0.25$. Since the eigenvalues of matrix B are in the range of -2 to $+2$, the fourth-degree polynomial is sufficient in Eq. (13). If we use Eq. (20) for the trace of matrix $|B|$, the equation for W_π becomes:

$$\begin{aligned} W_\pi = {} & 0{,}9637 m_{22}^1 + 0{,}9670 m_{22}^2 + 0{,}9682 m_{22}^3 + 0{,}7124 m_{23}^1 + 0{,}6948 m_{23}^2 + \\ & + 0{,}6833 m_{23}^3 + 0{,}6694 m_{23}^4 + 0{,}6187 m_{33}^1 + 0{,}5830 m_{33}^2 + 0{,}5606 m_{33}^3 + \\ & + 0{,}5562\, (m_{33}^{s\,int})_{cis} + 0{,}5555\, (m_{33}^{s\,int})_{trans} + 0{,}5830 m_{33}^{s\,ext} + 0{,}5405 m_{33}^{s\,int} + \\ & + 0{,}5514 m_{33}^{s\,ext} + 0{,}5343 m_{33}^{s\,int} + 0{,}5214 m_{33}^{s\,ext}. \end{aligned} \tag{21}$$

In this case we could not compare the results of calculations by this formula with exact values, owing to the lack of the latter in the literature.

Therefore, regardless of whether differences between β_{ij} and overlap integrals (for nearest neighbors) are introduced or not, in the approximation in question the structure of the expressions for the π-electron energy remains the

same: it is a linear function of the number of bond types characteristic for the given molecular series, with coefficients independent of the actual type of molecule. In other words, the π-electron energy in condensed aromatic compounds is the sum of the partial energy contributions of the individual bond types, i.e., it is an additive function.

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BRIEF COMMUNICATIONS

USE OF DENSITY DATA FOR ESTABLISHING THE STRUCTURE OF AQUEOUS ELECTROLYTE SOLUTIONS

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 604-607, September-October, 1961
Original article submitted June 1, 1961

The distance between an ion in aqueous solution and its nearest water molecules can, in a number of cases, be determined directly by the x-ray diffraction method. This distance, of course, depends on the specific interaction of the given ion with water molecules, but it can be assumed approximately equal to the sum of the crystal radius of the ion and the "radius" of the water molecule (1.4 A) [1,2]. The average distances between ions in solutions (for example, distances between like ions) are important in many problems of the theory of electrolyte solutions. As yet there is no method for direct experimental determination of these distances. These distances S_i depend mainly on interaction of the ions in solution, on the average number of water molecules between the ions (on the solution concentration), and on the density of their average distribution. At a given concentration the distances S_i are determined primarily by the distribution density of the water molecules in solution (of course, this does not apply to very high concentrations, when the water content of the solutions is low).

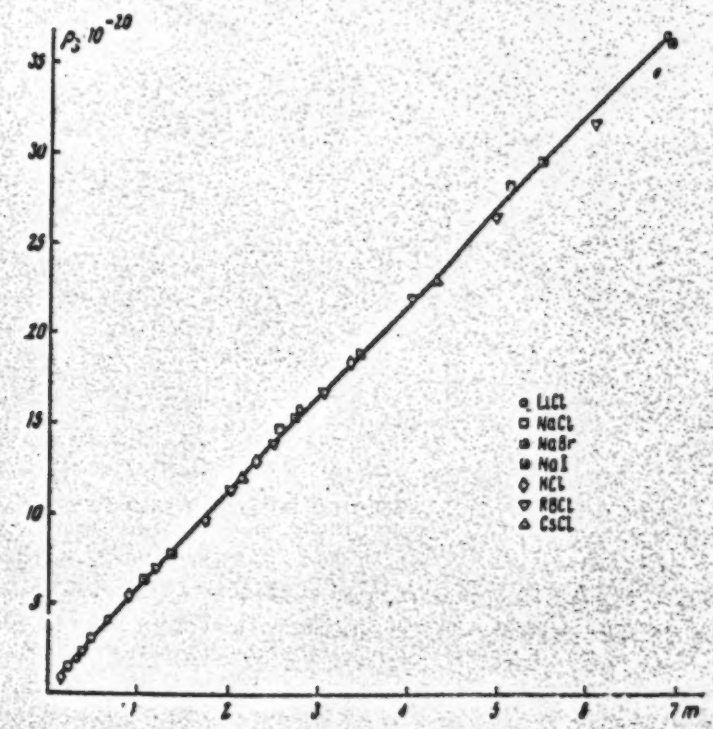

Fig. 1. Variation of ρ_S with m.

The average distribution density of particles in a liquid depends on the translatory motion of the particles. It has been shown that the greater the number of activated jumps of the particles in the liquid per unit time, the lower is their distribution density [3]. The average number of activated jumps performed by water molecules alters under the influence of ions. It was shown earlier [3] that this change is due mainly to the fact that the potential barrier between neighboring equilibrium positions of the water molecules becomes equal to $E + \Delta E_i$ near the ions, instead of E. The greater the value of ΔE_i (the greater the hydration of the ion), the less is the average number of activated jumps of water molecules nearest to the ions per unit time. Accordingly, the distribution density of water molecules should increase and the distance S_i should decrease with increase of ΔE_i. Conversely, the distance S_i should increase with decrease of ΔE_i (in particular, as ΔE_i changes from positive to negative values). This should in any case be valid for the region of not very low concentrations, where translatory motion of water molecules nearest to the ions is of relatively high importance. Moreover, at such concentrations filling of the cavities in the structure by water molecules, which occurs under the influence of ions and at low concentrations naturally leads to increased density, is of no significance [4]. It is therefore reasonably clear that at least in the region of moderate solution concentrations the values of S_i for a given concentration should be greater for CsCl than for LiCl solutions.* This conclusion is fully in agreement with the result obtained by Skryshevskii [2] in an x-ray investigation of aqueous electrolyte solutions; he concluded that the distance between the nearest water molecules not in coordination with ions is less than in pure water in the case of Li^+ cations, almost the same in the case of Na^+ cations, and greater in the case of K^+ cations.

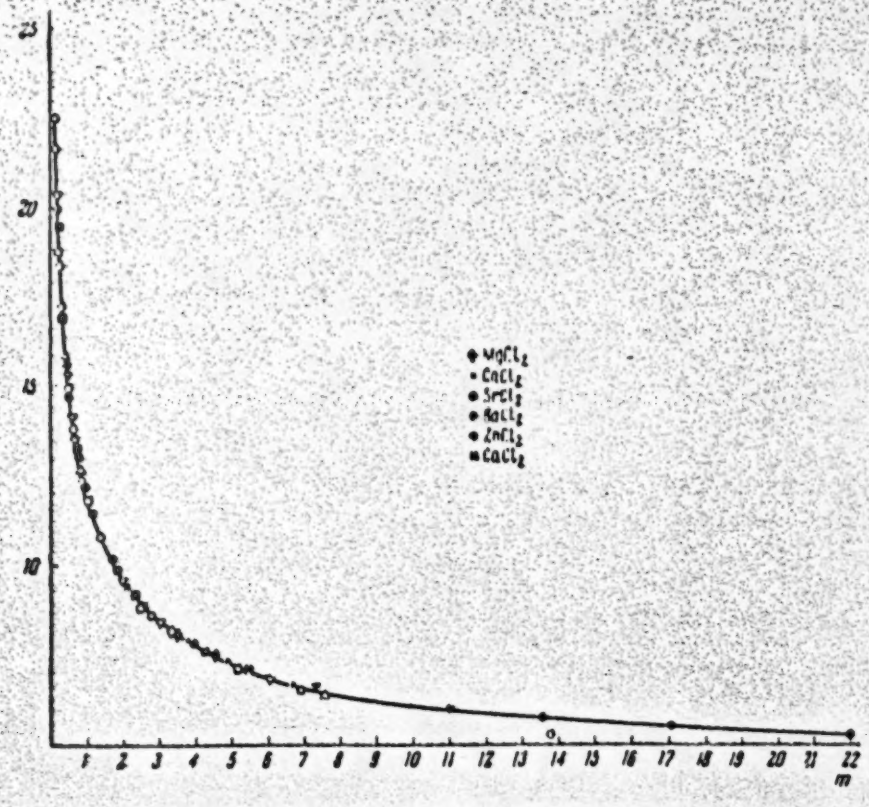

Fig. 2. Variation of S_i^* with m for chlorides of the second group (symbols as in Fig. 1).

It was of interest to find how these changes influence the densities of aqueous electrolyte solutions. We used the data given by Baxter and Wallace [5] for the densities of aqueous lithium, sodium, potassium, rubidium, and

*Increase of the ionic radii which accompanies decrease of ΔE_i should also change S_i in the same direction. However, the direct influence of the radii on S_i is probably relatively small, as S_i is greater than the distances between the nearest particles in solution.

cesium chloride solutions and of aqueous sodium bromide and iodide solutions (t = 25°). The solution volume V_m containing m moles (m is the molality of the solution) of the electrolyte was calculated:

$$V_m = \frac{mM + 1000}{d},$$

where M is the molecular weight of the salt, and d is the density of the solution in g/cm³.

The quantity $\rho_S = N_m / V_m$, where N is the Avogadro number, represents the density of the solution expressed as the number of like ions per unit volume (it is evident that ρ_S is proportional to the molar concentration of the solution). The values found for ρ_S are plotted against m in Fig. 1. It is seen that the values of ρ_S for salts with different cations and for salts with different anions differ very little at the same solution concentrations.

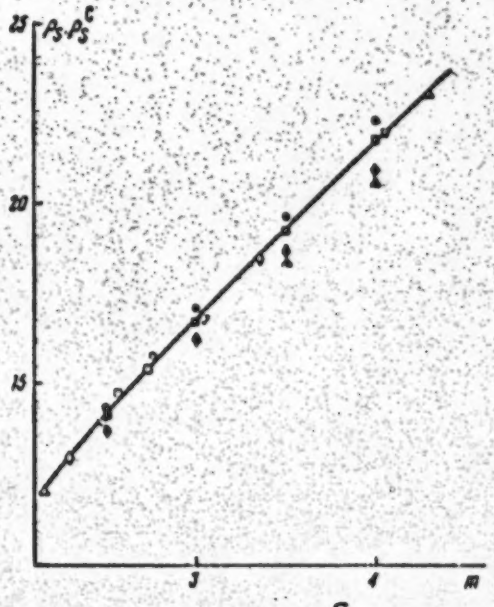

Fig. 3. Variations of ρ_S and ρ_S^C with m (values of ρ_S^C are indicated by black points).

On the assumption that the ions are distributed in solution to correspond exactly to a simple cubic lattice, the average distances between like ions are

$$S_i' = \sqrt[3]{V_m / Nm}.$$

The values of S_i' give an indication of the average distances between like ions in solutions. Values found for S_i' of chlorides of metals of group II of the periodic system are given in Fig. 2 [5,6].

Comparison of ρ_S values for different salts can be used for determining the character of the average ion distribution in solution.* In fact, the ρ_S values found for different salts at equal concentrations proved to be very similar. It follows that the numbers of particles per unit volume of aqueous solutions of different salts differ very little at the same concentrations. At the same time, the difference between the ionic radii, and especially the above-mentioned probable change of S_i under the influence of changes of ΔE_i, should lead to greater changes of ρ_S than are indicated by density data. For example, the change of ρ_S in the transition (at the same solution concentration) from lithium chloride to potassium chloride proves to be even less than the changes which should be observed in consequence of the difference of the cation radii only. This is clear from Fig. 3, where the calculated values of ρ_S are compared with ρ_S^C values calculated in accordance with the mixture rule (from the molar volumes of the crystals and the volume of water present in solution), and not found from experimental solution densities. The differences of ρ_S^C give an indication of changes in solution density due to changes of ionic radii only. It is seen in Fig. 3 that the differences between ρ_S due to the transition from lithium chloride to potassium chloride are considerably less than the corresponding ρ_S^C changes.

It seems that some sort of change in the character of the average arrangement of the particles takes place in solutions, compensating the density change due to translatory motion of the water molecules closest to the ions and to increase of the ionic radii. In view of the fact that at moderate and high solution concentrations filling of the cavities in the water structure by water molecules (highly significant at low concentrations) can hardly be of any importance, it must be assumed that this compensating change is associated with a change in the character of the average distribution of the ions in solution. Partial compensation may occur if decrease of ΔE_i (for example, in the transition from LiCl to CsCl solutions) is accompanied by a change in the character of the average ion distribution, in the direction of close packing. This is precisely the change which appears physically probable, because increase of the average number of activated jumps of the particles leads to a decrease of order, and therefore to a decrease of the role of directional bonds in solution.

*It is in no way assumed that order in solutions extends to large distances. The average distribution of ions in solution is characterized only in the sense of its difference (with respect to density) from the closest packing.

The foregoing considerations are probably of interest in relation to other systems in addition to aqueous electrolyte solutions. For example, a similar picture is obtained by comparison of ρ_S values calculated for lithium and ammonium nitrate solutions in acetamide. In connection with A. V. Kopellovich's paper, "Structural pressure of aqueous electrolyte solutions," [7], it is interesting to note that intensification of the translatory motion of water molecules closest to the ions leads to a change in the average distribution of the particles in solution in the same direction as does increase of external pressure.

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF RADICALS FORMED BY IRRADIATION OF POLYPROPYLENE

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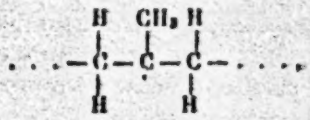
Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 607-609, September-October, 1961
Original article submitted April 8, 1961

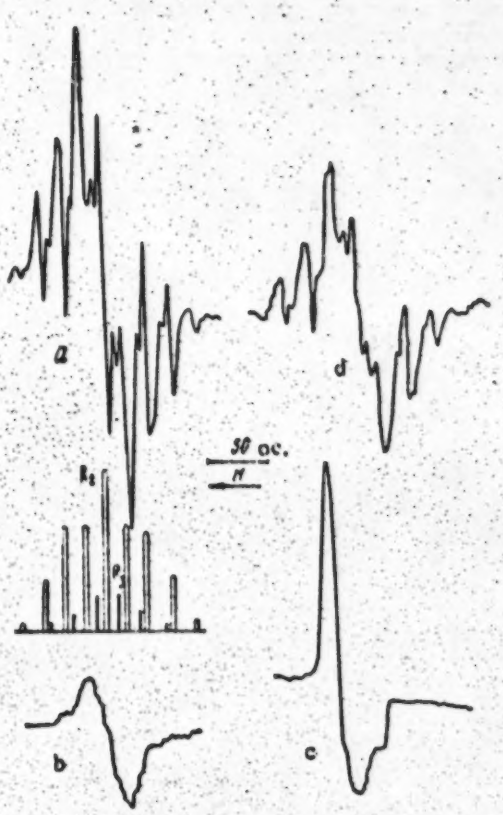
We have studied, under various conditions, the electron paramagnetic resonance (EPR) spectra of radicals formed during irradiation of polypropylene (PP) by Co^{60} γ-radiation of fast electrons. Powdered PP specimens of different degrees of crystallinity were used. In the earliest investigations of irradiated PP it was assumed [1] that the action of ionizing radiation results in the formation of a radical (R_1)



giving eight lines with binomial intensity distribution in the EPR spectrum. Such a spectrum is in fact obtained when PP is irradiated at 77°K. Its form remains unchanged when the temperature is raised to −78°, but at higher temperatures the spectrum changes irreversibly and at 25° it has the form shown in the figure (a). The higher the degree of crystallinity of the PP, the greater is the concentration of radicals stabilized at room temperature. When the temperature is lowered again, the components of the spectrum broaden reversibly, but their number and positions remain unchanged. The spectrum consists of 15 lines and may be regarded as the superposition of two spectra consisting of nine and six hyperfine structure components, respectively, with equal splitting between the components (about 20 oersteds). Both spectra disappear at the same rate on increase of temperature to 40-60°.

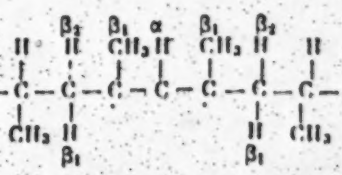
At room temperature the spectrum shown in the figure (a) undergoes further changes during several hours

(under vacuum). The signal intensity gradually diminishes and a broad line (about 40 oersteds) appears in the middle [see figure (b)]. When oxygen is admitted (at room temperature) the line of the peroxide radical appears [see figure, (c)]. We did not observe the substantial increase in the radical concentration which had been reported in the literature [2]. It is interesting to note that when the specimen had been kept at room temperature for several days oxygen did not produce any additional changes in the EPR spectrum.

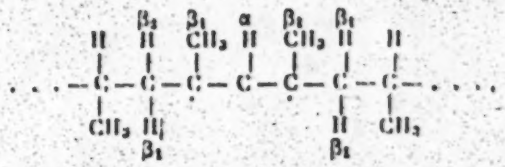


EPR spectra of radicals in irradiated polypropylene: a) polycrystalline specimen irradiated at 77°K and unfrozen (under vacuum) to 25°; b) specimen a kept under vacuum at 25° for 5 hr; c) specimen b 1.5 min after admission of oxygen; d) oriented specimen prepared as a; the magnetic field was perpendicular to the direction of chain orientation.

Our interpretation of these results is that at least four different radicals are detected by the EPR method in irradiated PP. By analogy with polyethylene [3] it is possible that after unfreezing we observe the spectrum of the allyl radical. Analysis shows that of the three types of allyl radicals which may be formed in the PP chain we should consider only the radical R_2, with the structure



It is assumed that the spin density at the central carbon atom is low; therefore splitting should be observed at eight equivalent β_1 protons (nine-component spectrum), while the orientation of the β_2 protons is such that they are not involved in the splitting. This hypothesis is in good agreement with the model of the isotactic PP chain which is now accepted [4]. The low-intensity even spectrum can then be ascribed to a small admixture of R_3 "isomers" of the form



in which, because of structural distortions of some kind, two protons of the CH_2 group on the right become equivalent and nine β_1 protons are involved in the splitting. Such radicals should be chemically equivalent, as is observed experimentally. Broadening of the components with lowering of the temperature is probably due to weak anisotropic interaction with the α proton. The appearance of a broad line after prolonged vacuum storage of the specimen may be attributed to the appearance of spectra of certain more stable radicals (in consequence of the disappearance of the spectrum of the allyl radical).

We also carried out measurements with oriented PP films. When the magnetic field is directed along the macromolecular axis, the EPR spectrum approximately coincides with the spectrum of a polycrystalline specimen, but the resolution is somewhat better and the relative intensity of the even spectrum increases. With increase of the angle θ between the direction of the external field and the orientation direction of the polymer chains, the breadth of the components increases, reaching a maximum at $\theta = \pi/2$, but the number and position of the lines remains unchanged [see figure, (d)]. This dependence of the EPR spectrum on the angle is consistent with the structure suggested above for the allyl radical, if it is assumed that the magnitude of hyperfine interaction at the α proton $A_\alpha \approx 0$ when the external field is perpendicular to the C – H bond, and $A_\alpha \approx 6$-8 oe when the field is parallel to it. For the radical R_1 the spectrum is not dependent on the angle, which is in harmony with the proposed structure of this

radical (there are no protons in the α-position). The observations described may be used in studies of the structure of polypropylene and of radiation-chemical processes taking place in it.*

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CRYSTAL-CHEMICAL DATA ON THE SALICYLALBUTYLIMINATES OF ZINC, COBALT, NICKEL, AND COPPER

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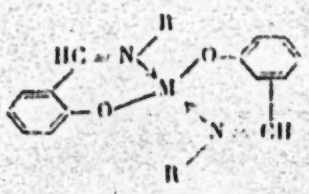
Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 609-612, September-October, 1961
Original article submitted June 16, 1961

The purpose of this investigation was to extend the available structural data on internal complex compounds of the type



Earlier x-ray structural investigations were concerned with salicylaliminates (R = H[1,2]), salicylalmethyliminates (R = CH_3[3,4,5]), and salicylaldoximates (R = OH[6,7,8]) of nickel and copper. In this investigation we studied the salicylalbutyliminates (R = n-C_4H_9) of Zn, Co, Ni, and Cu.

The substances were synthesized by the method described by A. P. Terent'ev and E. K. Rukhadze [9,10]; these workers prepared the Ni and Cu compounds. The synthesis of the Co compound is also described in the literature [11]. We did not find any references in the literature to the preparation of Zn salicylalbutyliminate.

The zinc compound after recrystallization consisted of white, very fine needles which split easily along the axis. The copper compound formed dark brown, large crystals of irregular shape, which were very often bent. The salicylalbutyliminates of Ni and Co were obtained in the form of well-defined single crystals, which were studied by the goniometric and x-ray diffraction methods. The results of the goniometric measurements were:

ρ	φ	Symbol	Simple form
	Cobalt salicylalbutyliminate		
0°	—	{010}	pinacoid
90°	0°	{100}	pinacoid
90°	30.6°	{101}	rhombic prism

*After this communication had been submitted for publication, we became acquainted with the investigation [5] in which analogous experimental results were obtained, but a different interpretation is offered for the EPR spectrum observed after unfreezing of the irradiated specimen.

μ	φ	Symbol	Simple form
49.1°	0°	{110}	rhombic prism

Nickel salicylalbutyliminate

90°	30.5°	{110}	rhombic prism
90°	40.0°	{210}	rhombic prism
30.5°	90.0°	{001}	pinacoid

The main method of investigation was by means of electron-diffraction patterns of specimens, obtained by evaporation of solutions, taken with the EM-4 electron-diffraction instrument. The lattice constants and space groups found from the electron and x-ray diffraction patterns are given in the table. The precision in determination of the constants depended on the quality of the photographs. The highest precision was obtained with the use of direct patterns from textures. The densities of Co, Ni, and Cu salicylalbutyliminates were determined by the flotation method; a concentrated $AgNO_3$ solution in which the crystal floated was diluted with water from a buret.

Analysis of the extinctions on the electron-diffraction patters of textures of the Zn compound leads to one of the following space groups: C2/m, Cm, Cmmm, C222, Cmm2, Cm2m; among these, only one does not contain mirror reflection planes. For the Zn salicylalbutyliminate molecules it is most reasonable to propose a tetrahedral model without a plane of symmetry. Such molecules cannot lie on m planes. If the molecules were arranged between the planes of symmetry, their packing would be very loose. Therefore, the only possible group is C222. In this case the Zn atoms occupy a fourfold position on twofold axes. This is in agreement with the tetrahedral model of the molecule. It must be noted that the position 4(i) with the coordinates 00z, 00$\bar{z}$, $\frac{1}{2}\frac{1}{2}z$, $\frac{1}{2}\frac{1}{2}\bar{z}$ [12] is impossible. With this arrangement there should be two Zn atoms on one twofold axis to one c period. The c period is too short for this.

The constants a and b of the Co salicylalbutyliminate unit cell, determined from the electron-diffraction pattern, are very close to the constants of the Zn compound, but c is six times as large. Evidently the structures of these compounds have much in common; this indicates that the structure of their molecules is similar. The cell constants of Co salicylalbutyliminate were also determined from x-ray oscillation patterns, obtained with iron radiation. Within the limits of experimental error the values of a and c coincide with the electron-diffraction data; the value found for b was 10.4 ± 0.2 A, which is half the value found from electron-diffraction patterns. One of the possible causes of this discrepancy may be the difference in structure between massive crystals and thin texturized films.

The electron-diffraction patterns of Ni salicylalbutyliminate showed the presence of two phases: 1) one giving a point orthogonal diffraction picture (phase 1), and 2) one with a tendency to form a texture (phase 2). X-ray oscillation patterns (copper radiation) showed single crystals to be identical with phase 1. It was shown with the aid of electron-diffraction patterns and the Weissenberg photograph of the h0$\bar{l}$ zero layer line that the space group of this phase is $P2_1/a$. With a twofold repeat the Ni atoms should be at the center of symmetry. It follows that the central group of the complex has planar structure and trans configuration.

Phase 2 was observed only in the electron-diffraction specimens. The intensities of the hk0 reflections were visually determined for this phase by the multiple-exposure method on a direct photograph of the texture. The P(uv0) Patterson projection showed that the Ni atoms are in a general position with the coordinates xyz, $\bar{x}\bar{y}z$; $\frac{1}{2}+x$, $\frac{1}{2}-y$, z; $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\bar{z}$, where x = 0.12, y = 0.27. Since the Ni atoms in phase 2 are not at the centers of symmetry, the molecules is noncentrosymmetric in this case [13]. This is possibly associated with the character of the deviation of the butyl group from the plane containing the rest of the molecule.

Only a point diagram was obtained by electron diffraction for Cu salicylalbutyliminate. However, in this case two types of photographs were again obtained; these probably correspond to two modifications (phases 2A and 2B). Both these modifications show a clear resemblance to phase 2 of Ni salicylalbutyliminate. If it is assumed that phase 2 of the nickel compound and phase 2A of the copper compound are isostructural and have the same monoclinic angle, it becomes possible to calculate two lattice constants of the 2A modification from the point electron-diffraction pattern. The good agreement of these constants with the corresponding constants of the nickel compound shows that these phases are in fact of very similar structure. Hence, it follows that phase 2A has four molecules in the cell and its space group is $P2_1/a$. Modification 2B differs from 2A first, in that the constant a is halved while b remains unchanged and, second, by the presence of $h + k \neq 2n$ extinctions among the hk0 reflections.

Structure Data on the Salicylalbutyliminates of Zinc, Nickel, Cobalt, and Copper

Compound	Crystal system	Cell constants					No. of molecules in cell	Density		Space group	Packing factor
		a, Å	b, Å	c, Å	β°	V, Å³		calc.	meas.		
Zn	rhombic	19,75 ±0,2	20,08 ±0,02	5,30 ±0,01	—	2100	4	1,35	—	$C222$	0,64
Co	rhombic	19,60 ±0,1	20,30 ±0,1	30,95 ±0,15	—	12300	24	1,33	1,30	$I222$ or $I2_12_12_1$	0,66
Ni (phase 1)•	monocl.	14,51 ±0,05	7,31 ±0,05	10,97 ±0,08	120,5±0,5	1000	2	1,36	1,33	$P2_1/a$	0,68
Ni (phase 2)	monocl.	17,30 ±0,04	5,34 ±0,02	22,30 ±0,2	93,9±0,3	2060	4	1,33	—	$P2_1/a$	0,66
Cu (phase 2A)••	monocl.	17,45 ±0,03	5,34 ±0,02	—	—	—	4	—	1,30•••	$P2_1/a$	—
Cu (phase 2B)	—	8,72 ±0,02	5,34 ±0,02	—	—	—	—	—	—	centered	—

•By x-ray diffraction method.

••Data obtained on the assumption that this 2A phase and phase 2 of the Ni compound are isostructural.

•••Measured for phase formed during crystallization in the vessel.

Packing density factors are given in the table; the molecular volumes were calculated with the aid of tabular values of interatomic distances, valence angles, and intermolecular radii [14], and results of structural investigations of internal complex compounds [1-8]. The values obtained are not very high. It is probable that this fact accounts for the existence of a whole series of polymorphic modifications; the molecular shape does not ensure the possibility of any particular close packing which would be preferable to the others.

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X-RAY STRUCTURAL INVESTIGATION OF $Co_2(C_5H_5)_5$

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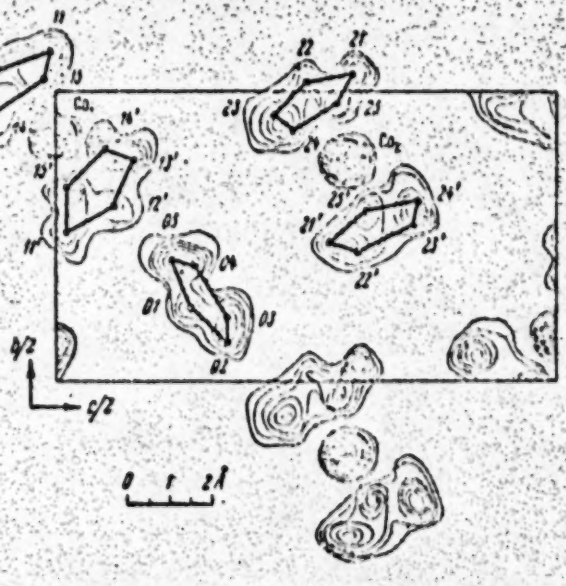
Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 612-614, September-October, 1961
Original article submitted June 5, 1961

In 1956, E. O. Fischer [1] briefly reported the preparation of a substance of the composition $Co_2(C_5H_5)_5$ by interaction of the cobalticinium cation with cyclopentadienylsodium. In 1960, at the request of Academician A. N. Nesmeyanov, Professor E. O. Fischer kindly supplied us with a sample of this substance for x-ray structural analysis.

The $Co_2(C_5H_5)_5$ sample consisted of rather large dark crimson crystals of prismatic form. The unit cell dimensions were: a = 5.83, b = 13.38, c = 23.74 (± 1% of the quantity measured). The unit cell contains four formula units of the composition $Co_2(C_5H_5)_5$. Systematic extinctions in the x-ray patterns obtained with a camera for photographing the reciprocal lattice (with unfiltered molybdenum radiation) showed that the $Pbc2_1$ or Pbcm space groups of the rhombic system are possible. Symmetry of the projections of a series of interatomic vectors showed conclusively that the crystals belong to the noncentrosymmetric $Pbc2_1 - C^5_{2v}$ space group.

Interpretation of the 0yz projection has now been completed. In interpretation of the projections of the interatomic vectors it proved possible to determine the coordinates of the heavy cobalt atoms. These were used for calculating the structure amplitude phases and the projection of the electron density on the same plane was constructed. As the maxima of about half the carbon atoms coalesced in this projection, geometrical analysis had to be used for establishing the coordinates of these atoms. The following considerations were taken into account. The electron-density projection (see figure) shows clearly that the "molecule" of the substance consists of three structural units; two "sandwich" units, each of which has a pair of five-membered carbon rings with a cobalt atom between them,

and a fifth carbon ring, also five-membered, which is not contained in the "sandwich" units. With the assumption that the length of the carbon–carbon bonds, in the "sandwich" units and the fifth ring is about 1.4 A (as is the case in ferrocene [2] and other analogous compounds), and with the form of the electron-density maxima in the projection taken into account, we can find the preferential positions of all the carbon atoms. To verify the correctness of this analysis, we determined the divergence factors, taking the theoretical values of the structure amplitudes first only for the cobalt atoms and then with all the atoms (except hydrogen) taken into account. In the first case R_{0kl} = = 35%, and in the second R_{0kl} = 25%; therefore, in the first approximation the coordinates of the carbon atoms were established satisfactorily. We then calculated two more approximations of the same electron-density projection, the phases being determined from the coordinates of all the atoms (except hydrogen), and in the last approximation the Booth correction for termination of the series was introduced. As a result, the divergence factor decreased to 16% (with the general isotropic temperature correction taken into account). The final projection is given in the figure. The atomic coordinates found from this projection are given in the table. In addition, the xy0 and x0z projections of the interatomic vector series were used for finding the third coordinates: $x_{Co_1} \approx 0.25$ and $x_{Co_2} \approx 0.75$.



Projection of the $Co_2(C_5H_5)_5$ electron density on the 0yz plane (final variant).

Analysis of the 0yz projection leads to the following conclusions. If we superpose on the electron-density projection of this compound the projection of ferrocene [2] (isomorphous with cobalticene [3]) along the short axis, very close in length to the short axis of the structure in question (5.95 A), we obtain almost complete correspondence of the projection of the ferrocene molecule with the "sandwich" particles of our structure (with superposition of the metal atoms and subsequent relative rotation of the projections until the best correspondence of electron densities is obtained). The ferrocene projection was used because the structure of cobalticene [3] has not been interpreted, but is fully analogous to the structure of ferrocene. Moreover, in the resultant projection the distances between the carbon atoms of the "sandwich" particles and the nearest carbon atoms of the fifth ring are found to be not less than 1.85 A, whereas the length of a single carbon–carbon bond does not in general exceed 1.55 A.

The foregoing facts lead to the conclusion that the $Co_2(C_5H_5)_5$ "molecule" consists of two "sandwich" $Co(C_5H_5)_2$ particles and a fifth C_5H_5 carbon ring, which does not have carbon–carbon bonds of the usual type with the "sandwich" particles. As a hypothesis of the structure of this compound, consistent with the results of the first stage of x-ray structural analysis, it may be postulated that the "sandwich" particles have formal charges of $+\frac{1}{2}$ each, while the fifth ring is the anion. It should be noted that Professor E. O. Fischer [4] reached similar conclusions on the basis of chemical and spectroscopic data.

Continuation of the x-ray structural investigation of $Co_2(H_5C_5)_5$ will make it possible to establish the $\underline{x}$ coordinates of all atoms, and thus to refine its geometrical structure; this should also be of considerable help for establishing the character of the bonds in this unusual compound.

Atomic Coordinates from the Final 0yz Electron-Density Projection*

Atom	y**	z	Atom	y**	z
C_{01}	0,1531	0,0000	C_{23}	0,088	0,218
C_{02}	0,2459	0,2800	C_{24}	0,140	0,236
C_{11}	−0,132	−0,084	C_{25}	0,051	0,282
C_{12}	−0,068	−0,055	C'_{21}	0,524	0,272
C_{13}	0,076	−0,097	C'_{22}	0,556	0,298
C_{14}	0,097	−0,068	C'_{23}	0,470	0,356
C_{15}	0,034	−0,011	C'_{24}	0,384	0,360
C_{16}	0,486	0,009	C'_{25}	0,420	0,309
C'_{11}	0,400	0,059	C_{31}	0,717	0,133
C'_{12}	0,238	0,078	C_{32}	0,866	0,167
C'_{13}	0,202	0,049	C_{33}	2,784	0,168
C'_{14}	0,346	0,013	C_{34}	0,604	0,137
C'_{21}	−0,050	0,293	C_{35}	0,587	0,113
C_{22}	−0,024	0,252			

*The numbering of the carbon atoms (see also the figure) is as follows: C_{1i} = atoms of the first five-membered ring, belonging to the first cobalt atom; C'_{1i} = atoms of the second carbon ring of the same "sandwich," taken by inversion of the cobalt atom from the corresponding atoms of the first ring; C_{2i} and C'_{2i} = the same for the second "sandwich"; C_{3i} = atoms of the fifth carbon ring.

**Values for the projected cell halved along the b axis.

The authors offer their deep gratitude to Professor E.O. Fischer of Munich University for kindly providing us with a sample of the substance for investigation and with the necessary data on its properties. We hope that this international cooperation in research on metal π-complexes will be continued and extended. The authors also wish to thank Academician A. N. Nesmeyanov and Professor A. I. Kitaigorodskii for their attention and interest.

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SOME STRUCTURE DATA ON CRYSTALLINE POLYVINYL CHLORIDE

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 615-616, September-October, 1961
Original article submitted April 25, 1961

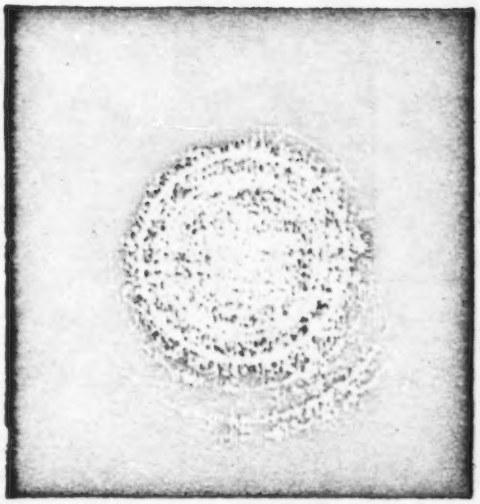
Much attention is now being devoted to synthesis of stereoregular polymers and to studies of their structure. Earlier [1] we described a method for preparation of crystalline polyvinyl chloride in presence of a heterogeneous catalytic system; the electron-diffraction pattern confirming the crystalline structure of the polymer contained ten sharp reflections. Recently, a brief communication [2] appeared in the literature on the preparation of crystalline polyvinyl chloride by free-radical homogeneous polymerization of vinyl chloride in aliphatic aldehydes at 50° in presence of azo compounds as reaction initiators. The x-ray patterns of nonoriented specimens of this polymer contained 13 rings with interplanar spacings between 5.16 and 1.14 A.

Interplanar Spacings of Crystalline Polyvinyl Chloride Specimens

Reflection No.	Data of [1] *		Data of [2]		Specimen 1 obtained in this investigation		Specimen 2 obtained in this investigation		Reflection indices hkl	$d_{calc.}$ A
	d, A	Intensity**	d, A	Intensity	d, A	Intensity	A	Intensity		
1	5.27	m	5.16	m	5.27	m	5.26	m	200	5.29
2	5.08	m	–	–	5.07	m	5.07	m	001	5.1
3	4.63	s	4.66	s	4.62	s	4.62	s	101	4.59
4	3.65	m	3.65	m	3.65	m	3.65	m	201	3.67
5	–	–	3.44	m	–	–	–	–	–	–
6	2.85	w	2.84	m	2.85	w	2.85	m	301	2.89
7	–	–	–	–	2.60	vw	2.62	w	400	2.64
8	–	–	2.56	w	2.52	vw	2.54	w	002	2.55
9	2.31	w	–	–	2.31	w	2.32	w	401	2.34
10	2.26	w	2.28	m	2.26	w	2.28	m	112	2.27
11	2.06	w	2.07	w	2.06	w	2.07	m	302	2.06
12	–	–	–	–	–	–	1.89	vw	510	1.92
13	1.82	vw	1.78	vw	1.82	vw	1.82	m	030	1.80
14	–	–	–	–	1.74	vw	1.74	w	230	1.71
15	1.69	vw	–	–	1.69	vw	1.69	w	131	1.69
16	–	–	1.59	vw	–	–	1.61	vw	203	1.61
17	–	–	–	–	–	–	1.54	w	303	1.53
18	–	–	–	–	–	–	1.44	w	132	1.45
19	–	–	1.40	vw	–	–	1.40	w	232	1.41
20	–	–	1.25	vw	–	–	1.21	w	440	1.21
21	–	–	1.14	vw	–	–	–	–	–	–

*Polyvinyl chloride prepared in presence of a heterogeneous catalytic system in saturated hydrocarbons with special complex-forming additives.

**s = strong, m = moderate, w = weak, vw = very weak



Electron diffraction study of polyvinyl chloride (specimen 2).

We used the method described in [2] for synthesizing crystalline polyvinyl chloride (specimen 1) in butyraldehyde in the temperature range from 0 to 60° with azoisobutyric dinitrile as initiator. The electron-diffraction patterns given by films of this polymer contain 13 sharp rings with d from 5.27 to 1.69 A. Rings with d = 1.74 and 1.69 A are not reported in [2], while rings with d = 5.07 and 5.27, 2.52 and 2.60, and 2.26 and 2.31 A are probably due to splitting of rings with d = 5.16, 2.56, and 2.28 A, found by x-ray diffraction [2]. We did not find the ring with d = = 3.44 A [2] by the electron-diffraction method.

We were able to show that addition of initiator to the reaction mixture is not essential for preparation of crystalline polyvinyl chloride. The catalytic system retains its stereospecific character in polymerization of vinyl chloride in the slightly oxidized aldehyde which contains, according to iodometric analysis, up to 0.03% of active oxygen. We were able to synthesize polyvinyl chloride of a high degree of crystallinity by this method (specimen 2, see table).

The electron-diffraction pattern of the twice-reprecipitated nonoriented specimen, crystallized at 120° during 2.5 hr (see figure) is exceptionally rich in reflections, containing 19 sharp rings. Here 13 of the reflections reproduce the observed interplanar spacings of specimen 1, while among the remaining 6 d can be determined reliably for 3 new reflections: 1.89, 1.54, and 1.44 A.

Comparative data on interplanar spacings for crystalline polyvinyl chloride prepared by various methods are summarized in the table.

It is interesting to note that in electron-diffraction investigation of polyvinyl chloride synthesized in presence of a heterogeneous catalytic system [1], all ten reflections found agree quite satisfactorily both in positions and in intensities with the corresponding reflections found in the present investigation.

It is noteworthy that the line with d = 3.44 A, detected in [2], does not appear on any of the electron-diffraction patterns of our crystalline polyvinyl chloride specimens, whereas, according to the relative intensities of all the reflections the line with d = 3.44 A, having moderate intensity, should inevitably appear in all the electron-diffraction patterns.

The literature [3] contains data on the crystal lattice of syndiotactic polyvinyl chloride, characterized by a rhombic unit cell with a = 10.6, b = 5.4, and c = 5.1 A. All the reflections of the electron-diffraction patterns are indexed relatively well on the basis of this cell. It should be noted that for the ring with d = 3.44 A [2] it is not possible to find a calculated interplanar spacing similar in magnitude which would correspond to any selection of reflection indices for this rhombic cell. Therefore, we consider the presence of a line with d = 3.44 A to be improbable.

Thus, in our opinion, the crystal lattice of polyvinyl chloride is characterized by 20 sharp reflections: the interplanar spacings for 19 of them are given in the table (specimen 2), while the 20th line, with d = 1.44 A, was detected by x-ray diffraction [2].

Since the electron-diffraction patterns of the polyvinyl chloride specimens studied are indexed quite satisfactorily on the basis of a lattice described in the literature [4], it seems that the crystal structure of our polymer coincides with the structure of the polymer investigated by Natta. However, these structures cannot be compared by their interplanar spacings because, in contrast to our work, Natta's paper contains values of d for oriented polyvinyl chloride specimens.

It should be noted in conclusion that the homogeneous catalytic system which was stereospecific for vinyl chloride was not stereospecific for polymerization of other vinyl polymers such as styrene, methyl methacrylate, and vinyl acetate; the polymers were found to be amorphous. In all probability the cause of formation of crystalline polyvinyl chloride by radical polymerization of vinyl chloride should be sought in the structure of the complexes, consisting of aldehyde and vinyl chloride, which are formed as the result of dipole interaction between monomer molecules and solvent molecules.

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HARDNESS OF TRANSITION-METAL NITRIDES

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 617-618, September-October, 1961
Original article submitted October 15, 1960

Nitrides of refractory transition metals are of considerable technical interest as components of heat-resisting alloys, special refractories, and surface coatings resistant to corrosion and wear [1]; moreover, investigations of their physical properties are important for indirect elucidation of the peculiarities in the electronic structure of these compounds, which have a considerable proportion of ionic bond character, owing to the high ionization potentials of the nitrogen atom [2]. One such physical property is the hardness, which has hardly been studied in the case of nitrides, apart from data on the microhardness of titanium and zirconium nitrides published in [3] and [4].

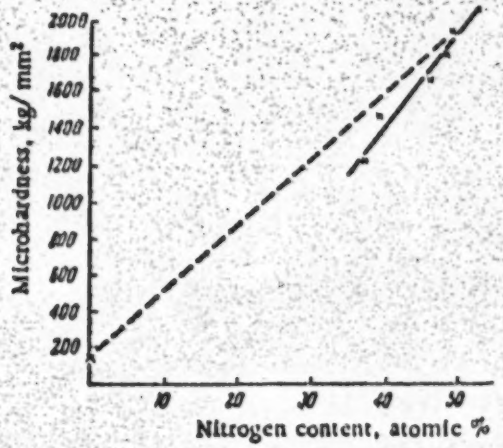

Fig. 1. Microhardness of titanium nitride in the homogeneity region.

In this investigation we performed systematic measurements of the microhardness of nitride phases of titanium, zirconium, vanadium, niobium, tantalum, and chromium; the specimens were prepared by direct nitriding of the metal powders under conditions excluding simultaneous oxidation, by the method described in detail in [5]. In the case of titanium nitride variations of microhardness with concentration were also determined in the homogeneity region which, according to literature data, extends at least from 30 to 50 atomic % [1]. All the microhardness determinations were carried out with a load of 50 g on the indentor of the PMT-3 instrument. The results are given in the table.

Microhardness of Nitride Phases of Titanium, Zirconium, Vanadium, Niobium, Tantalum, and Chromium

Phase	Nitrogen content, %		Microhardness kg/mm²	Phase	Nitrogen content, %		Microhardness, kg/mm²
	by wt.	atom.			by wt.	atomic	
$TiN_{0.59}$	14,7	37,1	1200±137	$VN_{0.74}$	16,8	42,4	1520±115
$TiN_{0.63}$	15,7	39,1	1440±182	$NbN_{0.46}$	6,6	31,7	1720±100
$TiN_{0.85}$	19,9	46,1	1630±101	$NbN_{0.96}$	12,7	49,1	1396±26
$TiN_{0.92}$	21,4	47,9	1780±51	$TaN_{0.58}$	4,3	36,6	1220±120
$TiN_{0.97}$	22,2	49,3	1900±182	$TaN_{1.01}$	7,3	50,29	1060±72
$ZrN_{0.91}$	12,3	47,8	1480±85	$CrN_{0.47}$	11,2	32,0	1571±49
$VN_{0.338}$	8,5	25,3	1900±102	$CrN_{0.99}$	21,0	49,8	1083±93

The microhardness of titanium nitride in the homogeneity region is a linear function of concentration (Fig. 1) and, in this respect, it is analogous to the microhardness of the carbides of titanium [6], zirconium [7,8] and

ntalum [9] as a function of the combined carbon content. However, whereas in the latter three cases extrapolation f the microhardness graph to zero carbon concentration gives the approximate microhardness values of the respect- ve metals, this is not so in the case of titanium nitride. It follows that the character of the electronic structure and electron-density distribution in carbides differs little from that of metals, as has already been reported [10, 11]. In nitrides, on the other hand, it alters, probably owing to the appearance of a considerable proportion of ionic bonding; as Fig. 1 indicates, this proportion increases with decrease of nitrogen content in the nitride lattice. This result may be due to formation of Me – Me bonds, lesser perturbation of the valence electrons of the nitrogen atoms, and a corresponding increase in the break between the s- and d-states of titanium and the p-states of nitrogen. The width of the energy "gap" at low nitrogen contents becomes sufficient to confer semiconductor properties to titanium nitride; this was shown experimentally in [15].

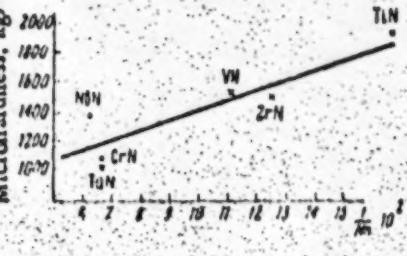

Fig. 2. Variation of the microhardness of mononitrides with the acceptor capacity of transition-metal atoms.

In Fig. 2 the microhardness of mononitrides is plotted against the acceptor capacity of transition-metal atoms, expressed by the factor $1/Nn$, where N is the principal quantum number and n is the number of electrons in the incomplete d-level. Despite the considerable scatter, due mainly to the fact that differences of crystal structure are not taken into account (niobium, chromium, and tantalum mononitrides have hexagonal lattices, while those of titanium, zirconium, and vanadium mononitrides are cubic face-centered), it is clearly seen that the hardness increases with increasing acceptor capacity of transition-metal atoms; this is associated with the decrease in the proportion of ionic bonding and a more uniform distribution of electron concentration. There is also some correlation between the microhardness values and the factor of the Lindemann equation, determining the vibration frequency of linear oscillators (Fig. 3); this is understandable in view of the similarity of the processes in fusion and in hardness determinations, as was pointed out by Born, and noted in relation to interstitial phases in [12] and [13].

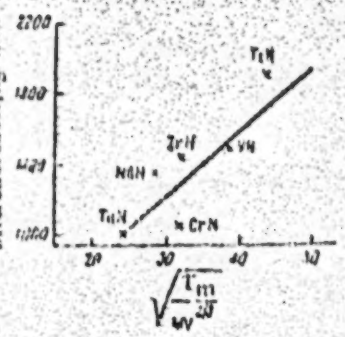

Fig. 3. Variation of the microhardness with $\sqrt{\frac{T_m}{MV^2}}$.

At the same time, it should be noted that there is no correlation between nitride hardness on the one hand, and lattice energies, atomization energies, and specific surface free energies on the other.

It is also noteworthy that the hardness of the lowest nitride phases is considerably higher than the hardness of mononitrides; this may be explained, by analogy with the concepts in [14], by substantial strengthening of Me – Me bonds with decrease of the relative number of interstitial nitrogen atoms in phases of limiting composition.

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LETTERS TO THE EDITOR

STRUCTURAL MOTIFS OF NICKEL AND COPPER DIALKYL GLYOXIMATES

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
p. 619, September-October, 1961
Original article submitted May 20, 1961

In the review of the present state of the crystal chemistry of complex compounds [1], owing to condensation of the original text during preparation of the manuscript, I made an unfortunate error which distorts the data of Frasson and Panattoni on the crystal structure of nickel and copper methylethylglyoximates [2]. However, comparison of the structural motifs of these compounds and of the related dimethylglyoximates is of undoubted interest for illustration of the peculiarities of the stereochemistry of nickel and copper in "open" complexes.

The nickel dimethylglyoximate crystal [3] is built up of planar molecules located in parallel planes so that the Ni atoms are above each other at distances of 3.245 A, forming infinite Ni – Ni – Ni . . . chains. In the nickel methylethylglyoximate crystal the molecules are shifted in their own planes so that opposite the Ni atom of one molecule there is on each side an oxygen atom of a neighboring molecule at a distance of 3.44 A (the Ni – Ni distances increase to 4.75 A). In other words, the competition between two types of additional interaction, "metal – metal" and "metal . . . ligand – metal," leading to formation of molecular chains, is resolved here in favor of the second type. It seems that the Ni – Ni and Ni . . . O – Ni interaction energies are very similar, and the choice between the two motifs is determined by changes in the packing density when methyl groups are replaced by ethyl.

In the structure of copper dimethylglyoximate [4] the molecules are located over each other with a shift, as in the case of nickel methylethylglyoximate. However, the interaction between copper and oxygen atoms of neighboring molecules is apparently stronger than the analogous Ni – O interaction; the Cu . . . O distance shortens to 2.43 A and the molecule itself ceases to be planar. As a result, the molecular chain splits up sharply into dimers. According to preliminary data [2] an analogous change in comparison with the nickel compound is observed in copper methylethylglyoximate.

Thus, in the nickel compounds in question, the coordination number of the metal atom is 4 + 2, the two additional bonds arising as the result of Ni – Ni interactions in the one case, and as the result of Ni – O interactions in the other, while in copper compounds the coordination number is 4 + 1, the fifth bond arising as the result of Cu – O interaction.

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CONCERNING THE PAPER BY M. A. PORAI-KOSHITS AND P. M. ZORKII: "STRUCTURE RELATIONSHIPS OF INTERNAL COMPLEX COMPOUNDS OF COPPER AND NICKEL"

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 619-620, September-October, 1961
Original article submitted April 20, 1961

The first number of Zhurnal Strukturnoi Khimii for 1961 contains a paper by M. A. Porai-Koshits and P. M. Zorkii [1] dealing with certain structural characteristics of internal-complex compounds (ICC) of copper and nickel. In this paper the authors extend one aspect of our paper [2]: "the arrangement of copper atoms in general positions in a number of cases when the nickel atom in internal complex compounds with the same ligands occupies a special position is apparently not accidental but is associated with the fact that the molecule can deviate to a greater or lesser extent from a planar structure," and consider in detail its applicability to all the ICC groups given by us.

We are in full agreement with the first three conclusions reached by M. A. Porai-Koshits and P. M. Zorkii [1] in their consideration of the experimental data. These conclusions coincide with the findings in our 1959 [2] and 1954 [3] publications. However, in our opinion, the fourth conclusion, based on the data in Table 3 [1] is erroneous, as this table requires correction. 1) The data given in this table on the phthalocyanides of nickel and copper and on the nickel phthalocyanide analog are superfluous. They cannot serve as the basis for deducing the configuration of the metal atom, as this configuration may be enforced in these cases and depends on the geometry of the ligand. 2) Data on the methylethylglyoximates of nickel and copper [4], later than those given in Table 3, show that in these ICC copper atoms are in a general, and nickel atoms in a special, position, i.e., the molecule of the nickel ICC is centrosymmetric, and that of the copper ICC is noncentrosymmetric. When these corrections are introduced into Table 4 the data on ICC of the M – 4N group become as definite as the data on ICC in the M – 4S and M – 4O groups.

As the experimental data available at present are limited, the conclusions put forward with regard to deviations of copper and nickel ICC from planar configuration can be based, at best, on only a few examples, and in certain groups of ICC on only two examples; for example, there are two nickel compounds in the M – 4O group with noncentrosymmetric molecules, two copper compounds in the M – 4S group, and again two copper compounds in the M – 4N group. Such conclusions must be based merely on probabilities. According to the data in Tables 1, 2, and 4, and in the amended Table 3, we have the following general statistics at the present time: with nonisostructural ICC of copper and nickel the absence of a center of symmetry (the metal atom is in a general position) is found in five cases for molecules of copper ICC and in two cases for molecules of nickel ICC. Moreover, in the ICC group M – 2N, 2O (cis), all the nickel compounds are diamagnetic and have planar structure [1]. Deviations from planar structure may be expected among the copper compounds, as they are not isostructural with the corresponding nickel compounds [1]. Therefore, data on ICC of the M – 2N,2O (cis) group reinforce these statistics.

Therefore, even if "it cannot be asserted that nonplanar complex structure is characteristic for copper, as distinct from nickel" ([1], our italics), it is permissible to suppose that nonplanar complex structure is more characteristic for copper than for nickel.

We consider that with this approach it is quite possible to "conclude to what extent the nonisostructural character of copper and nickel ICC crystals is typical" [1]. In our opinion, classification of substances by the composition of the direct environment of the metal atoms, which we also used in [2] and [3], is appropriate enough and may help in the correct interpretation of the problem under consideration.

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REPLY TO THE LETTER BY E. A. SHUGAM AND L. M. SHKOL'NIKOVA

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 620-621, September-October, 1961
Original article submitted June 3, 1960

We must agree with the authors of the letter that the data on copper and nickel methylethylglyoximates given in Table 3 of our paper require correction. Unfortunately, we were not aware of the results of the complete structural investigation of these compounds, published only a short time before our paper had been submitted for publication. We also agree that the configuration of the environment of the metal atom in phthalocyanides cannot be regarded as characteristic. Data on phthalocyanides were included in Table 3 for the sake of completeness.

However, even with all this taken into account, the data on ICC of the M – 4N group are not of less definite character than data on ICC in the M – 4S and M – 4O groups. The point is that in all the examples know to us, Cu atoms are at centers of symmetry in the M – 4O group, and outside the centers of symmetry in the M – 4S group. At the same time, in the M – 4N group we know examples both of centrosymmetric (α-pyrrolaliminate) and noncentrosymmetric (dimethylglyoximate, methylethylglyoximate) arrangements of Cu atoms.

E. A Shugam and L. M. Shkol'nikova rightly point out that the experimental data available at this time are rather meager. We also referred to this in our paper. Nevertheless, classification of ICC by the composition of the environment of the metal atoms already makes it possible to draw tentative conclusions concerning the structural characteristics of ICC belonging to different groups. If nonplanar coordination is in fact characteristic of Ni in the M – 4O group and of Cu in M – 4S and M – 2N,2O (cis) groups, then the statistics for the entire class of four-coordinated ICC as a whole must be determined only by the relative number of structural investigations performed for compounds of different groups.

THEORY AND PRACTICE OF DIRECT METHODS OF STRUCTURE ANALYSIS OF CRYSTALS*

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 622-639, September-October, 1961
Original article submitted December 22, 1960

The theoretical principles of various direct methods for determining the signs of structure amplitudes are considered: reliable relationships in the form of determinants and inequalities, exact equations connecting structure factors, and statistical methods without and with symmetry elements taken into account. Examples of the use of various methods by Soviet workers are given. In conclusion, certain new theoretical investigations by Karle and Hauptman and by others are considered.

1. Introduction

Most structural investigations are carried out at present with the aid of interatomic vector series, proposed by Patterson as long as 25 years ago. Despite the considerable success achieved by crystallographers in recent years in developing new variants of this method, interest in searches for other methods of structure analysis has always remained high. We must not ignore the fact that interpretation of Patterson series for structures of atoms of equal weight already becomes problematical when the number of atoms in general positions exceeds 5-10, and there can no longer be any question of direct analysis. It becomes necessary to postulate structure models, compare them with the Patterson series, look for explicit signs of the proposed model in the series, or else reject the given hypothesis.

A direct method of structure analysis is one for which we do not require information on structure, and therefore one in which we do not use structural models postulated on the basis of experimental chemical crystallography. In order not to be unduly rigorous, we shall apply the term "direct" to methods in which only information on the number and kind of atoms in the unit cell are used. With this definition the method of Patterson series is a direct method only in the very simple cases; for example, for a molecule with one heavy atom.

The direct methods we shall discuss are methods for direct determination of the signs or phases of structure amplitudes based only on experimental data on x-ray reflection intensities (therefore we do not touch upon methods based on minimalization analysis of the Patterson function, etc.).

It must be remembered that the number of x-ray reflections is often many times the number of parameters determining the structure. Suppose, for example, that 1000 structure amplitudes are recorded for 20 atomic coordinates; this means that the amplitudes are not independent quantities and can be expressed in terms of each other. Another way of saying this is that with 20 independent coordinates there are only 20 independent structure amplitudes, and all the others can in principle be expressed in terms of these 20.

*Revised text of a paper presented on August 19, 1960 at the Fifth Internation Congress of Crystallographers in Cambridge.

Another important fact is specific for x-ray structure analysis. Since x rays are scattered by electron density, the Fourier series having structure amplitudes as coefficients must give positive density values at all points in the unit cell. It is clear that this fact also leads to the existence of connections between the structure amplitudes.

2. Reliable Connections between Structure Amplitudes

Attention to the possibility in principle of devising direct methods was first drawn by Banerjee [1] and Avrami [2] even in the 1930's. However, the methods they proposed were unsuitable for practical use and did not attract attention. It is no exaggeration to say that the history of the development of direct methods of structure analysis begins with the work of Harker and Kasper [3], who established the existence of a very wide class of inequalities connecting the magnitudes of the structure amplitudes of some reflections with the signs of others [4,5]. As the result of the work of Karle and Hauptman [6], Goedkoop [7], and later of Kitaigorodskii [8], it was shown that the Harker–Kasper inequalities are the consequence of one general theorem, based on the nonnegative character of electron density, whereby the various relationships between structure amplitudes can be expressed in very elegant form.

A proof of this theorem, which mathematicians call the Herglotz theorem [9], may be found in the works cited in this paper. The essential content of this theorem is as follows: we select in a reciprocal lattice (m − 1) random points H, K, L, M, . . . , write the individual structure amplitudes of these points and also of K − H, L − H, M − H... L − K, M − K..., and construct the nth order determinant

$$D_m = \begin{vmatrix} 1 & \hat{F}_{-H} & \hat{F}_{-H} & \hat{F}_{-L} & \cdots \\ \hat{F}_H & 1 & \hat{F}_{H-K} & \hat{F}_{H-L} & \cdots \\ \hat{F}_K & \hat{F}_{K-H} & 1 & \hat{F}_{K-L} & \cdots \\ \hat{F}_L & \hat{F}_{L-H} & \hat{F}_{L-K} & 1 & \cdots \end{vmatrix} \qquad (1)$$

It is found that this determinant cannot be negative:

$$D_m \geq 0. \qquad (2)$$

The inequality becomes an equation if m > N (N is the number of atoms in the unit cell).

Kitaigorodskii [10] showed that the practical applicability of this equation, which may be called the fundamental equation for structure amplitude relationships, depends sharply on the absolute values of $\hat{F}$ in the determinant. The following simple rule holds: If none of the amplitudes in the determinant is greater than $1/(m-1)$ (m is the order of the determinant), then no information about signs is obtainable from the equation. For example,

$$\begin{vmatrix} 1 & \cdots & \cdots \\ \hat{F}_H & 1 & \cdots \\ \hat{F}_K & \hat{F}_{K-H} & 1 \end{vmatrix} > 0, \quad \text{if all} \quad \hat{F} < 1/2.$$

$$\begin{vmatrix} 1 & \cdots & \cdots & \cdots \\ \hat{F}_H & 1 & \cdots & \cdots \\ \hat{F}_K & \hat{F}_{K-H} & 1 & \cdots \\ \hat{F}_L & \hat{F}_{L-H} & \hat{F}_{L-K} & 1 \end{vmatrix} > 0, \quad \text{if all} \quad \hat{F} < 1/3.$$

etc.

Thus, analysis is useless for a determinant of the third order when $\hat{F} < 1/2$, of the fourth when $\hat{F} < 1/3$, of the fifth when $\hat{F} < 1/4$, etc.

The possibilities of using low-order determinants can be represented by means of diagrams [10]. As an example, the diagram in Fig. 1 shows variations in the signs of the H + K and H − K amplitudes with their absolute values for the cases when $|\hat{F}_H| = 0.5$ and $|\hat{F}_K| = 0.1$. It is easy to see that certain ranges of $\hat{F}_{H+K}$ and $\hat{F}_{H-K}$ values are excluded. It is important to note that in certain regions $\hat{F}_{H+K}$ is positive and $\hat{F}_{H-K}$ is negative, and these are regions where both $\hat{F}_{H+K}$ and $\hat{F}_{H-K}$ are large. The signs of structure amplitudes can be determined with the aid of diagrams similar to Fig. 1. It must be remembered, however, that the greater the number of atoms in the cell (i.e., the more complex the structure), the smaller are the values of the "strongest" structure amplitudes and the less effective are these diagrams and other variants of the direct method.

Analysis of determinants of high orders is excessively complicated and hardly feasible in practice. However, since it is possible to make up a very large number of such determinants for a given structure, it is quite probable that all the relationships between structure amplitudes can be derived by means of determinants (possibly with the aid of computers).

In practice it is usually more convenient to use reliable relationships in the form of Harker–Kasper inequalities [3], and inequalities put forward by others [4,5] which are easily programmed for computers. It should be noted that the above-mentioned criterion $\hat{F} > 1/(m-1)$ for the validity of determinants does not coincide with the validity region of the corresponding inequalities.

3. Exact Equations Connecting Structure Amplitudes

A characteristic feature of the Harker–Kasper inequalities and of the more general relationships given by the determinants is that they contain a relatively small number of structure amplitudes and the result is a limitation of their magnitudes and signs.

There is, however, another system of equations which contains all the structure amplitudes. We refer to the Sayre equation. If we represent the electron density $\rho(x)$ by a Fourier series, and then find an analogous function, such as $\rho^2(x)$, and also represent it by a Fourier series, then we can equate (or compare) the corresponding Fourier coefficients and thereby find the relationships between them.

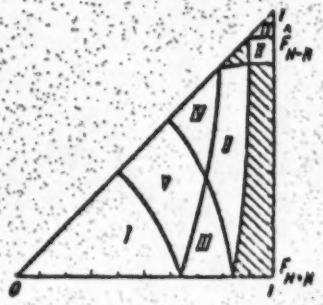

Fig. 1. Diagram representing interdependence of signs when $|\hat{F}_H| = 0.5$ and $|\hat{F}_K| = 0.1$. I) Signs not determined; II) $\hat{F}_{H+K} > 0$, $\hat{F}_{H-K} < 0$; III) $\hat{F}_{H+K} > 0$; IV) $\hat{F}_{H+K}$ and $\hat{F}_{H-K}$ have different signs; V) $\hat{F}_{H+K}$ and $\hat{F}_{H-K}$ are of the same sign, and $|\hat{F}_{H+K}| > |\hat{F}_{H-K}|$. Impossible regions are shaded.

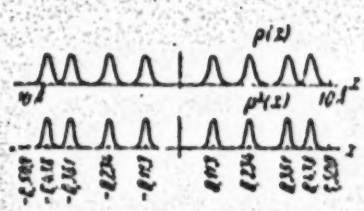

Fig. 2. Hypothetical unidimensional structure of like atoms, and its square, used by Sayre for verification of his equation.

This was the procedure adopted by Sayre, who drew attention to the fact that if the structure consists of atoms of the same kind, the $\rho^2(x)$ is similar to $\rho(x)$ in all respects with the exception of the form of the peaks: the "squared" atomic functions have more concentrated electron distribution (Fig. 2). This difference is easily eliminated if the corresponding atomic factors are taken into account: f for $\rho(x)$ and g for $\rho^2(x)$.

In order to find the Fourier coefficients for the square of the structure, we must perform an operation widely used in structure analysis, namely convolution, which consists of finding the sum (or integral) of the product of the two relatively shifted original functions, i.e., in this case the combination of structure factors. The shift in which we are interested is performed in reciprocal space, by a certain vector H':

$$F_{\rho^2}(H') = \frac{1}{V}\sum_{H} F_{\rho}(H)\, F_{\rho}(H - H'), \qquad (3a)$$

where the coefficients of the Fourier series for the original function $\rho(x)$ are on the right, and the Fourier coefficient of its square $\rho^2(x)$ is on the left. However, since $F_{\rho^2} = \frac{g}{f} F_{\rho}$, we can continue the above Eq. (3a), obtaining as a result:

$$\sum_{H} F(H) \cdot F(H - H') = \frac{g}{f} F(H'). \qquad (3b)$$

This is the Sayre equation, which provided the impetus to an extensive series of investigations of statistical sign relationships: the Zachariasen–Cochran equations, and many others. The Sayre equation is valid for structures of atoms of the same kind whatever the symmetry; it is also valid for projections if the atoms in them are not superposed.

B. K. Vainshtein [12] drew attention to the fact that a $\sigma_0(x,y)$ projection of the crystal structure can be obtained, not only by the usual method from the zero-plane reflections F(hk0) of the reciprocal lattice, but also from the F(hkL) reflections of nonzero layer lines, where L = const. Reflections of the second type lead to the so-called generalized projections $\sigma_{\cos L}(xy)$ and $\sigma_{\sin L}(xy)$, the "peaks" on which may be either positive or negative. However, by combining the sine and cosine weighted projections we can always obtain the positive modulus projection

$$|\sigma_L(xy)| = \sqrt{\sigma^2_{\cos L}(xy) + \sigma^2_{\sin L}(xy)}. \qquad (4)$$

If we now eliminate (which can be done very simply) the difference between the atomic factors of the zero and the L-th layer line, we have, in general

$$\sigma_0(xy) \geq |\sigma_L(xy)|, \tag{5}$$

and if the atoms in the projections are not superposed, then

$$\sigma_0(xy) = |\sigma_L(xy)| \quad \text{and} \quad \sigma_0^2 = \sigma_L \sigma_L^*. \tag{6}$$

The squares of the respective functions are equal. An example of the quantity of σ_0 and σ_L is given in Fig. 3 for the structure of diketopiperazine (investigated by electron diffraction [13]).

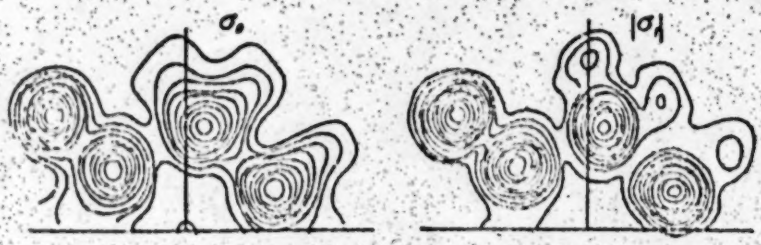

Fig. 3. The usual σ and modulus $|\sigma_0|$ projections of the potential of the diketopiperazine structure.

Performing the convolution operation and equating the respective Fourier coefficients, we have

$$\sum_{hk,L=0} F(hk0)\, F^*(h-h', k-k', 0) = \sum_{hk,L=\text{const}} F(hkL)\, F^*(h-h', k-k', L). \tag{7}$$

It follows that convolution of structure amplitudes for a plane network of a reciprocal lattice is invariant for any hk vector, i.e., its value is the same for any L. Equation (7) is valid for structures of any symmetry (including noncentrosymmetric) and remains accurate in presence of atoms of any kind (not necessarily all alike). If the atoms are superposed in the projection, Eq. (7) is transformed into inequalities, which may be written not only for planes but also for parallel straight lines of the reciprocal lattice. It is interesting to note that, since the squares of the functions are compared, the usual condition that $\sigma(r)$ is not negative is not applied, and Eq. (7) is also valid for neutron diffraction analysis when the atomic functions may be negative.

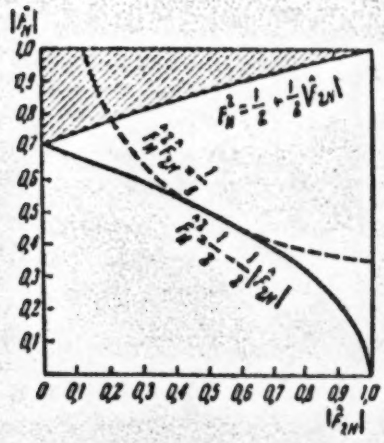

Fig. 4. Consequence of the simplest Harker–Kasper inequality (limited by continuous lines) and the simplest structure product (limited from below by the broken line).

However, this high degree of generality is attained at high cost – both sides of Eq. (7) contain convolutions, whereas one side of the Sayre equation (3) simply contains the value of F_H. Therefore, the nonnegativity condition is not, in general, obligatory in determination of relationships between structure amplitudes, but a very valuable possibility is obtained when it is applied – it is possible to connect products (or powers) of F_H with their first powers.

Returning to Eq. (7), we may note that its conversion into an inequality when atoms overlap makes it possible to interpret certain cases of the inapplicability of the Zachariasen relationship when nonzero layer lines are used.

The Sayre equation and the Vainshtein relationships are not used in practice at the present time because they include a very large number of structure amplitudes in contrast, for example, to inequalities or statistical equations involving two to four structure amplitudes. However, these exact equations, which are of theoretical significance, may find practical application in the future.

4. Properties of the Structure Product

On the basis of the Sayre equation, Zachariasen [14] and Cochran [15] showed that the sign of $\hat{F}_{H+K}$ predominantly coincides with the sign of the product $\hat{F}_H\hat{F}_K$.

Kitaigorodskii [16] considered the quantity $\hat{F}_H\hat{F}_K\hat{F}_{H+K}$, which was named the structure product. It is easy to show that the sign of the structure product is independent of the coordinate origin chosen. It is then possible to formulate the Zachariasen–Cochran law as a law which states that the structure product is predominantly positive. Consequently,

$$\text{sign of } F_H = \overline{\text{sign of}(F_K \cdot F_{H+K_i})}\ K_i. \tag{8}$$

The sign of F_H predominantly coincides with the sign of $F_H \cdot F_{H+K_i}$, i.e., predominantly

$$F_H F_K F_{H+K} > 0. \tag{9}$$

What is the basis for this law? Karle and Hauptman [17] and Kitaigorodskii [10] showed that the predominantly positive character of $\hat{F}_H\hat{F}_K\hat{F}_{H+K}$ follows from the uniform distributions of the arguments of the trigonometric functions. These authors derived formulas for the probability that the sign of the structure amplitude should be positive. However, this explanation of the law of the predominantly positive character of the structure products is very incomplete and is valid only for the region of low structure products, which is of less practical interest. Kitaigorodskii [16] drew attention to a simple property of the structure product of strong structure factors:

$$x = \hat{F}_H\hat{F}_K\hat{F}_{H+K} > 0, \text{ if } |x| > \frac{1}{8} \ldots \tag{10}$$

Thus, all structure products exceeding $\frac{1}{8}$ are reliably positive. It is found that this property, like the law of the predominantly positive character, can also be derived from the determinant of the connection between structure amplitudes. Although the applicability range of Eq. (10) is somewhat narrower than that of the corresponding simplest Harker–Kasper inequality (Fig. 4), the equation is extremely simple to use.

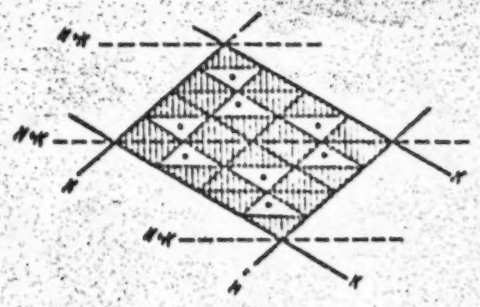

Fig. 5. Applicability regions of the Zachariasen equation (shaded).

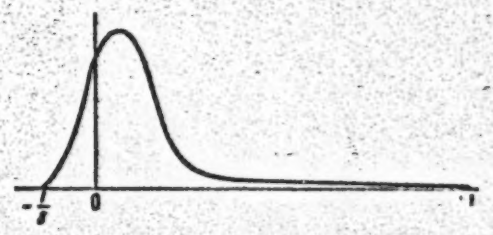

Fig. 6. Distribution function for the structure product.

The simplest geometrical interpretation of the positive character of the structure product was given by Golovastikov and Belov [18]. If we draw the family of $hkl = H$ and $h'k'l' = K$ planes in the cell (Fig. 5), then the planes of the $H + K$ (or $H - -K$) family pass through the intersection points of the planes of the first two families. It is known that the straight lines in this figure may be regarded as the "vertices" of the sinusoidal harmonics of the electron density, corresponding to the F_H, F_K, F_{H+K}, F_{H-K} structure amplitudes. We now place one atom in an independent region of a noncentrosymmetric cell (i.e., two atoms per cell), and move it all over this region. Simple calculation shows that the expression

$$s_H s_K = s_{H+K} \text{ or } s_{H-K} \quad (s = \text{sign})$$

is valid over 75% of the area of the figure for any values of F_H, F_K, $F_{H \pm K}$ (the validity regions are shaded). The highest negative value of the structure product $\hat{F}_H\hat{F}_K\hat{F}_{H \pm K} = -\frac{1}{8}$ is attained at the centers of the white triangles. Consequently, this simple example vividly demonstrates the rule that if the structure product is greater than $\frac{1}{8}$, it must be reliably positive. It is easy to show on the same geometrical considerations that increase of the number of atoms lowers the probability that the equation is valid, whereas increase of the moduli $\hat{F}$ raises it. "Unidimensional" geometrical interpretation makes it possible to find certain strong statistical equations, such as $s_{2H} = s_H s_H 2_H$. This approach was subsequently developed in [19].

The character of the distribution function of the structure product is shown in Fig. 6. It must be emphasized that only the central portion of this curve representing the law of the predominantly positive character of the structure

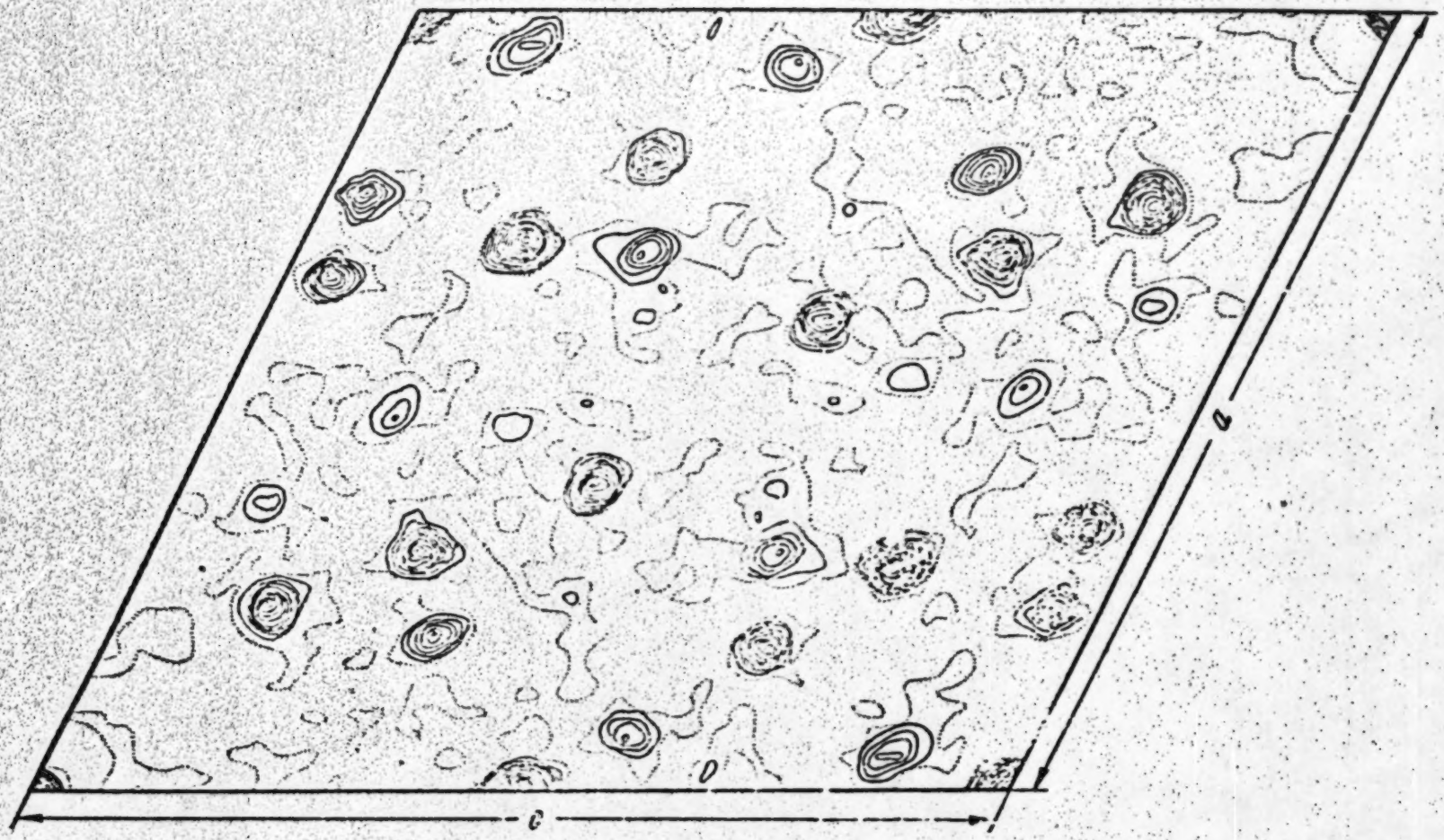

Fig. 7. Electron density projection of epidote.

TABLE 1.

Mineral	Cell constants and space group	No. of atoms in cell	No. of structural parameters	e	No. of nonzero reflections	No. of signs determined by direct method	Condition for reliable sign determ.	% of signs correctly determined
Epidote $Ca_2Al_2FeSi_3O_{12}(OH)$	$a = 8{,}89$ Å $b = 5{,}62$ Å $c = 10{,}23$ Å $\beta = 115°24'$ $P2_1/m$	42	35	0,19 ($h0l$)	350	293	$P \geqslant \frac{2}{3}$	100
Eremeevite $AlAlB_2O_{13}(OH)_2$	$a = 8{,}54$ Å $c = 8{,}16$ Å $P6_3/m$	58	18	0,18 ($hk0$) 0,15 ($h0l$)	175 186	175 186	$P > 0{,}5$ $P > 0{,}5$	90 86
Xonotlite $Ca_6Si_6O_{17}(OH)_2$	$a = 16{,}5$ Å $b = 7{,}33$ Å $c = 7{,}03$ Å $\beta = 90°$ $P2/a$	64	45	0,19 ($h0l$)	202	167	$P \geqslant \frac{2}{3}$	94
Herderite $CaBePO_4F$	$a = 9{,}80$ Å $b = 7{,}08$ Å $c = 4{,}80$ Å $\beta = 90°06'$ $P2_1/a$	32	24	0,20 ($hk0$) 0,19 ($h0l$)	167 116	140 90	$P \geqslant 0{,}7$ $P \geqslant 0{,}7$	100 100

product is the consequence of the uniform distribution of the arguments of the trigonometric functions of the structure amplitudes. The "tail" of the curve, which is of the main importance in application of the law of predominantly positive character, is in no way associated with the random distribution of the atomic coordinates, but is the consequence of the fundamental equation for the connection between the structure amplitudes. Therefore, the law of the predominantly positive character is valid for the simplest as well as for complex structures.

5. Practical Application of the Statistical Method

The law of the predominantly positive character (8), (9), which is a statistical law, is so simple that it is naturally very desirable to use it for practical purposes of structure analysis. Determination of signs with its aid is known as the statistical method.

This method is applicable in practice if the signs of a large enough group of structure amplitudes (known as the basic group) are known. These signs can be determined, for example, from inequalities or from reliable structure products. It is then necessary to find a sufficient number of $\tilde{F}_H\tilde{F}_K$ pairs from the basic group which, without contradictions or with the minimum number of contradictions, lead to as yet unknown $\tilde{F}_{H+K}$.

This method has considerable chances of success if the root mean square value of a single structure factor is

$$\sigma = (\Sigma n_j^2)^{-1} > 0{,}2. \qquad (11a)$$

If we consider a structure of N-like atoms, when

$$\sigma = 1/N, \qquad (11b)$$

then $\sigma > 0{,}2$ corresponds to $N < 25$. Sometimes σ can be increased by introduction of heavy atoms into the structure; this often extends the potentialities of the method. For example, this method was used for determining the structure of $HgCl_2 \cdot$ coumarin [20], for which $\sigma = 0{,}18$; the investigation reported in [20] was the first successful application of direct methods in the Soviet Union. With lower values of σ, success in the use of this variant of the direct statistical method becomes a matter of chance and depends also on the intuition of the investigator. However, the magnitude of σ should not be regarded as an absolute criterion of the resolvability of the structure, since the specific features of a particular structure (symmetry, kinds of atoms, order in their arrangement, etc.) may play the greater part in structure determinations by direct methods. The problem cannot be solved if an error creeps into the determination of the signs of the basic group at the first stages of the investigation. Several workers met with failure of this kind when attempting to apply direct methods to relatively complex structures. However, successful attempts are also known.

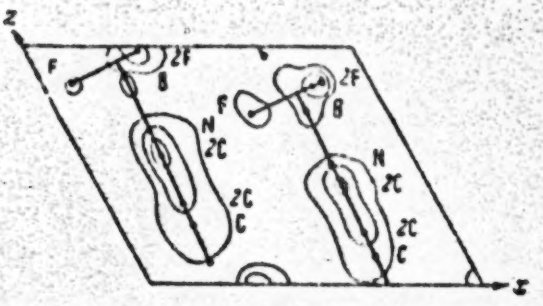

Fig. 8. Electron density projection of $F_3B \cdot NC_8H_9$.

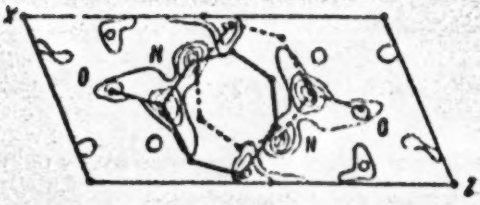

Fig. 9. Electron density projection of caprolactam.

After the investigation reported in [20], practical applications of direct methods in the Soviet Union were started in the laboratory of Academician N. V. Belov, in the Institute of Crystallography of the Academy of Sciences of the USSR. Complex inorganic silicate structures were investigated.

In 1953 Belov and Rumanova [21] determined the structure of epidote $Ca_2FeAl_2O(OH) \cdot [Si_2O_7][SiO_4]$. This monoclinic structure, with $P2_1/m$ symmetry, contains 42 atoms in the cell and is described by 35 parameters. Attempts to apply the Patterson method did not give the desired results owing to overlapping of the light O atoms in the x0z projection, corresponding to the shortest distance b. However, this also made it easier to apply the direct method, since the effective number of atoms in the projection was diminished to $N_{pr} = 30$. With 350 nonzero F_{h0l} it was possible, with the aid of Harker–Kasper inequalities, to determine the signs of 70 reflections with the greatest individual amplitudes. On this basis, with the aid of the Zachariasen–Cochran–Sayre statistical relationship [8], it was possible to extend the basic group to 125 reflections and then to determine the signs of 168 more amplitudes. The groups of three structure factors H, K, and H + K were found by the method proposed by Vainshtein, involving superposition onto the

simplified network of the reciprocal lattice of a transparent copy of it with a shift by the vector H; this makes the points H + K and K coincide. The signs found for the 293 F_{h0l} structure amplitudes were used for plotting the $\sigma(xz)$ electron density projection shown in Fig. 7, which reveals the arrangement of all the atoms very clearly. A complete interpretation of the epidote structure was possible on the basis of the $\sigma(x,z)$ diagram.

This was followed by determinations of structures of roughly the same complexity – eremeevite, xonotlite, wollastonite, herderite, gadolinite, and datolite [22-25] (see Table 1, in which data on the use of direct methods for interpretation of some of these structures are summarized). Xonotlite is characterized by a pronounced pseudoperiod $b' = b/2 = 3.77$ A, because of which it was possible to consider a cell of half the size, with N = 32. The Harker–Kasper inequalities were used for determining the signs of 62 F_{h0l} out of 202 nonzero F_{h0l}. The great majority of the remaining F_{h0l} were then found statistically; the number of determining relationships for each sign quite often exceeded 20. The $\sigma(x,z)$ diagram was then plotted and a model of the structure was derived from it; the structure was represented by the formula $Ca_6[Si_6O_{17}](OH)_2$ and not $Ca_3Si_3O_8(OH)_2$, as was formerly believed. Turning to the other minerals detailed in Table 1, we see that, although the structures contain several dozen atoms each, superposition of the atoms in the projections, the presence of atoms of different kinds, and also of pseudoperiods in some instances, lead to values of σ of the order of 0.2; this ensured success of the inequality method.

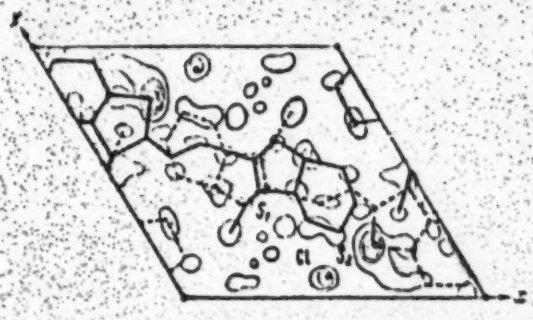

Fig. 10. Electron density projection of $[C_{21}H_{21}N_2S_2]^+Cl^-$.

A characteristic feature of the interpretation of these structures with the aid of projections was the absence of any symmetry elements with the exception of inversion centers. Therefore, the results of sign determinations by the inequality method could be expressed by three letters and the "+" sign, whereas the "–" sign could not be obtained directly. The letter symbols used to denote the signs according to the evenness (or oddness) of the indices are:

Evenness (or oddness) of indices h, k	$2n, 2n$	$2n, 2n+1$
Sign	+	a
	r	ar
$2n+1, 2n$	$2n+1, 2n+1$	
b	ab	
br	abr	

In accordance with the known rules for arbitrarily chosen signs [17, 26, 27], any sign (for example, plus) could be ascribed to two of the letters; this predetermined the choice of the coordinate origin at one of the four centers of symmetry of the projection. The sign of the third letter had to be "guessed"; as was to be expected, it was negative in all the cases studied (otherwise all the signs would be positive).

In the laboratory of the L. Ya. Karpov Physicochemical Institute in Moscow, Zhdanov, Zvonkova, and their co-workers are using direct methods for analysis of organic structures. The following criterion for sign determination was established empirically: the Zachariasen statistical relationship holds if at least one of the absolute structure amplitudes in it exceeds 0.25. Of the two structure products $\hat{F}_H\hat{F}_K\hat{F}_{H+K}$ and $\hat{F}_H\hat{F}_K\hat{F}_{H-K}$ only one is taken, with $\hat{F}_{H+K}$ or $\hat{F}_{H-K}$, according to which is the greater in absolute magnitude:

$$s_{H+K} = s_H s_K, \text{ if } |\hat{F}_{H+K}| > |\hat{F}_{H-K}|$$
$$s_{H-K} = s_H s_K, \text{ if } |\hat{F}_{H+K}| < |\hat{F}_{H-K}| \quad (12)$$

The structures were determined from two projections. First two arbitrary signs and three letter symbols for the signs were taken. This gave 75% and over of correctly determined signs. This procedure was used for investigating a number of compounds differing in complexity: realgar [28], the boron trifluoride–pyridine complex, caprolactam, and others [29, 30].

The $F_3B \cdot NC_5H_5$ unit cell contains eight molecules and the general fourfold position of the $P2_1/c$ space group is occupied by two atoms. Correct results were obtained for 82% of the signs of the structure amplitudes of the F_{h0l} type. The electron-density projection based on the results of the direct method is given in Fig. 8. All the atoms of the structure are clearly revealed.

Figure 9 shows the $\sigma(xz)$ electron-density projection of caprolactam; the signs of the amplitudes for its calculation were determined by the direct method. The unit cell contains eight molecules having the configuration of nonplanar seven-membered rings and including the amide group. The projection immediately revealed two caprolactam molecules joined by a twofold screw axis. Owing to errors in signs of the amplitudes there are four superfluous maxima of small magnitude.

TABLE 2.

Structure	Cell constants	Space group	No. of mol. in cell	No. of atoms in cell	σ	No. and type of reflection	No. of signs determ.	% of signs correctly determ.
Realgar As_4S_4	$a = 9,27$ $b = 13,50$ $c = 6,56$ $\beta = 106°37'$	$P2_1/c$	4	32	0,18	112 ($hk0$) 71 ($h0l$)	106 62	80
$F_3B \cdot NC_5H_5$	$a = 17,7$ $b = 5,89$ $c = 14,34$ $\beta = 118°40'$	$P2_1/c$	8	80	0,12	112 ($h0l$)	90	87
Caprolactam $C_5H_{10}CONH$	$a = 19,2$ $b = 7,65$ $c = 9,4$ $\beta = 113°$	$C2/c$	8	64	0,13	70 ($h0l$) ≈ 1000 (hkl)	70	78
$[C_{11}H_{21}N_4S_2]^+Cl^-$	$a = 12,4$ $b = 11,7$ $c = 10,8$ $\alpha = 90°$ $\beta = 113°$ $\gamma = 122°$	$P\bar{1}$	2	78	0,14	120 ($hk0$)	120	77

TABLE 3.

Mineral	Cell constants and space group	No. of atoms in cell	No. of structure parameters	σ	No. of non-zero reflec.	No. of signs determ. by the direct method	Condition for reliable sign determination	% of signs correctly determined
Zoisite $Ca_2Al_3Si_3O_{12}(OH)$	$a = 16,20$ Å $b = 5,50$ Å $c = 10,14$ Å $Pnma$	84	34	0,13 ($h0l$) 0,12 ($hk1$)	407 277	275 212	$P \geq \frac{2}{3}$	99 98,5
Cuspidine $Ca_4Si_2O_7F_2$	$a = 7,53$ Å $b = 10,41$ Å $c = 10,83$ Å $\beta = 60°56'$ $P2_1/c$	60	45	0,15 ($h0l$) 0,19 ($0kl$) 0,15 ($hk0$) 0,14 (hkl)	211 244 151 2500	144 190 120 1500	$p \geqslant 0,7$	99 97 97
Astrakhanite $Na_2Mg(SO_4)_2 \cdot 4H_2O$	$a = 11,03$ Å $b = 8,14$ Å $c = 5,40$ Å $\beta = 100°39'$ $P2_1/a$	34	24	0,19 ($hk0$) 0,18 ($hk1$) 0,20 ($h0l$)	152 245 155	135 228 146	$p \geqslant 0,6$	93 93 92

Because of the complexity of the triclinic structure of the dye 3,3-diethylthiocarbocyanine chloride, the cation of which contains 25 atoms (not counting the hydrogen atoms), it was studied simultaneously and independently by the direct method and with the aid of the interatomic vector function. The σ(xy0) electron-density projection based on the direct method is given in Fig. 10. Two cations joined through the center of symmetry, and two chloride ions can be seen. The direct method made it possible to determine the coordinates of three semiheavy atoms (S_1, S_2, and Cl) and 14 light atoms.

General data on the structures investigated by Zhdanov and Zvonkova and their co-workers are contained in Table 2. This table shows that relatively complicated structures can be solved by the statistical method. Although some of the signs are wrongly determined, the Fourier synthesis reveals nearly all the atoms. The errors influence the form of the peaks and displacements of the latter from the true positions do not exceed 0.1 A.

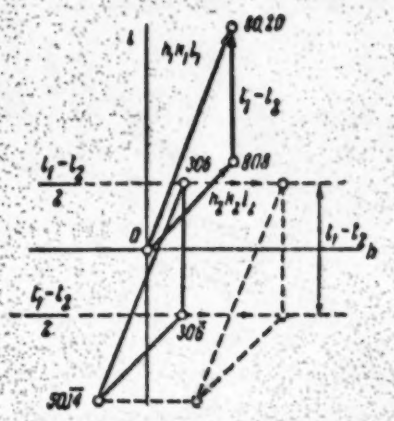

Fig. 11. Schematic representation of sign determination by the comparison method. The reflections being compared are 80.20 and 808; the determining reflections lie along the horizontal broken line, forming the same geometrical pattern in the reciprocal lattice as those being compared; $s_{hkl} = s_{hkl}$ with h = 2n, $s_{hkl} = -s_{hkl}$ with h ≠ 2n.

6. Relationships between Structure Amplitudes Due to Structure Symmetry

The potentialities of the statistical method are extended considerably if we take into account the structure symmetry which establishes the relationships between the phases of the structure amplitudes. This is the basis of the "comparison method" developed by Rumanova in 1954 [31, 32]. Later an analogous but somewhat more cumbersome procedure was described by Grant, Howells, and Rogers [33].

The idea of taking microsymmetry into account is very simple and clear. In the usual method for using the statistical equation, groups of three structure amplitudes (H_1, H_2, and $H_1 - H_2$) are compared, and it is assumed that their structure product is probably positive. If symmetry is taken into account, each sign of two structure amplitudes s_{H_1} and s_{H_2} is repeatedly expressed in terms of products of pairs of signs $s_{H_i}s_{H_j}$ of the other (determining) structure amplitudes:

$$s_{H_1} = s(\overline{s_{H_i}s_{H_i}}), \qquad s_{H_2} = s(\overline{s_{H_i}s_{H_j}}). \tag{13}$$

Here the signs of the determining pairs for s_{H_1} and s_{H_2} are connected by symmetry conditions, so that the relationship (identity or difference) between the signs s_{H_1} and s_{H_2} is also established. Rumanova's simple technique [32] (Fig. 11) makes it possible to select such determining pairs from all the numerous reflections. The greater the values of the moduli $|\tilde{F}_H|$ of the individual structure amplitudes, the higher is the probability that these statistical relationships hold; therefore, reflections with highest $|\tilde{F}_H|$ should be chosen for comparison and as the determining values. For example, it proved possible to find seven such determining pairs for the structure of zoisite for the 808 and 80.20 reflections (Fig. 11). The first of these showed that the signs of these reflections are different:

$$s_{808} = s_{206} \times s_{80.14} = s_{206} \times s_{80.14}$$
$$s_{80.20} = s_{206} \times s_{80.14}$$

Of the seven pairs, five gave the same result, while the opposite result was obtained in the other two cases; therefore, the signs of the 808 and 80.20 reflections were taken as opposite with a "probability" of 5/7.

In the comparison method the values of the individual structure amplitudes may be considerably less than the values needed for the inequality method because, although the probability of error in an individual comparison may be greater, the total error must be greatly diminished on statistical grounds.

The relationships found between the individual compared signs of the basic group are then used for obtaining "chains" of signs. Figure 12 shows some of these chains for the zoisite structure. Connecting the chains by means of the Zachariasen–Sayre relationship, and taking the signs fixing the coordinate origin arbitrarily [25-27], we find the basic group which is then used for determining the signs of the remaining reflections by the same Zachariasen–Sayre statistical method.

The structure of zoisite [32], cuspidine [34], and astrakhanite [35] were determined by this method. A summary of data on these structure determinations is given in Table 3, where the main information on interpretation of these structures is given in addition to the chemical formulas and cell constants. Thus, in the case of the complex silicate zoisite, with 84 atoms in the cell, the signs of the F_{h0l} and F_{hll} structure amplitudes were determined. It was therefore possible to plot the usual and generalized projections, which gave the complete picture of the structure.

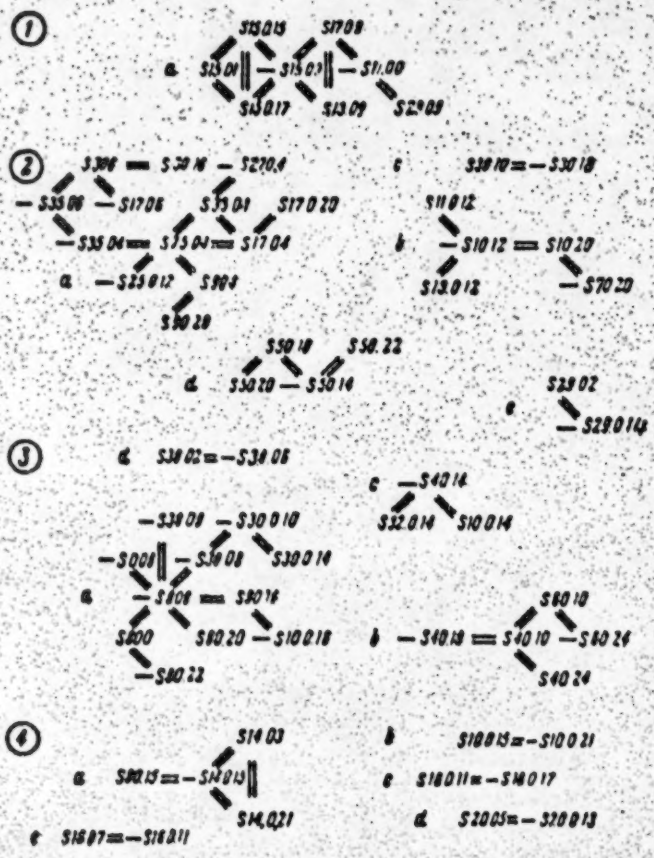

Fig. 12. Chains of signs for the h0*l* zone of the zoisite structure.

In determination of the structure of cuspidine it was necessary to determine the signs of about 1500 out of 2500 reflections of the general hk*l* type in order to find the signs of three projections. This bulk of data was necessary owing to structural peculiarities, as the majority of reflections with odd h indices were weak. Figure 13 shows the σ(xy) electron-density projection of cuspidine; the peaks are pronounced and "ghosts" are virtually absent.

The structure of astrakhanite was determined similarly [35]. Evidence that the interpretations were correct is provided by the low values of the divergence factors (for example, for astrakhanite R = 10%) in addition to the usual crystallographic criteria and "purity" of the syntheses.

It is clear from Table 3 that with symmetry taken into account it is possible to progress toward investigations of more complex structures, and this variant does not require reduction to an absolute scale. It should be noted that this method is especially effective if the atoms forming the structure differ little in atomic number, if the symmetry of the structure is not high (thombic, monoclinic), and in absence of atoms in positions without parameters.

7. Calculation of Phases from Intensity Data

In the first publications dealing with the theory of direct methods much attention was devoted to calculations of the distribution function of the structure product; the probability that the sign of the structure product is positive was calculated with its aid. Fruitful work was done in this field by Karle and Hauptman [6, 7, 36, 37], Bertaut [38, 39], Kitaigorodskii [8, 10, 15], Cochran and Woolfson [14, 40-42], Vand and Pepinsky [43], Klug [44], and many others, who used a variety of mathematical approaches.

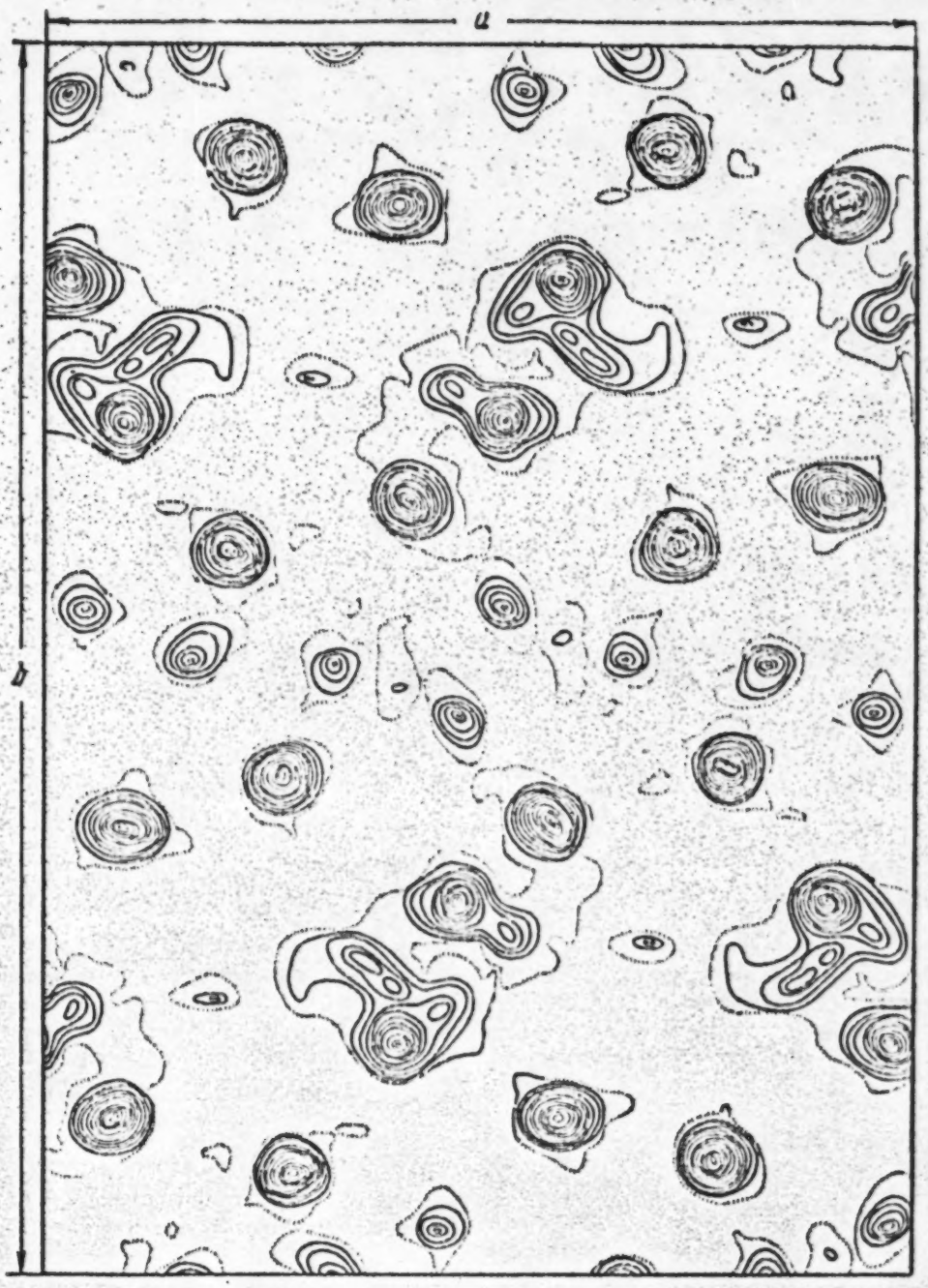

Fig. 13. Electron density projection of cuspidine.

Unfortunately, being able to calculate the probability that the sign of the structure product will be positive does not take us further forward in the practical sense. It is easy to calculate from the formulas now available that there is an ultimate probability of a negative value for very strong structure products of the order of 0.05-0.07. By taking the strongest possible structure products at the first stage of the investigation we risk making an error even if the probability formulas give a reassuring value of the order of 99%.

The direct procedure, examples of which were given above, does not in general require a knowledge of probability formulas at all. Moreover, it is obvious that it is impossible to devise a faultless scheme of direct analysis on the basis of probability considerations.

What kind of formulas would solve the problem of direct methods? The problem would be solved if we could formulate equations whereby it is possible to express any structure amplitude or structure product in terms of intensities of the measured reflections. Calculation of structure products leading to correct signs, even if not to accurate values, would provide a complete solution of the problem of structure analysis of noncentrosymmetric crystals.

We have seen with the example of the derivation of the Sayre equation that the relationships for direct methods can be obtained by comparison of certain functions, such as ρ, ρ^2, etc., in real space. This proposition is of general character, as was pointed out by Cochran and Woolfson [42].

We do not consider here methods for determining structures from the Patterson P(r) function; the reader is referred to [45, 46]. However, using the idea of functions for determining the structure from the picture of interatomic vectors (for example, the "total," "product," etc.) we can find expressions for determining the signs without finding these functions as such. This possibility was first pointed out by McLachlan and Harker [47], and it was subsequently analyzed by Simonov and Vainshtein [48]. Suppose that having found in the picture of the F^2 series the coordinate of the $2r_0$ peak joining the noncentrosymmetric atoms, we perform the shift and find the product function $\Pi(r) = P(r + r_0)P(r - r_0)$. This function is similar to the P(r) function; therefore, the Fourier coefficients in their expansions are probably of the same sign. This sign is essentially determined by all the values of F^2_{hkl} and the coordinate of one atom r_0:

$$s(F_H) \approx s \sum_{H'} ((F^2_{H'} \cdot \cos 2\pi H' r_0)[F^2_{H-H'} \cdot \cos 2\pi (H - H') r_0] + (F^2_{H'} \sin 2\pi H' r_0)[F^2_{H-H'} \cdot \sin 2\pi (H - H') r_0]). \quad (14)$$

A test of this expression for the complex structure of the mineral seidozerite [48] gave the following result: out of 378 amplitudes the signs of 36 were wrongly determined, i.e., 90.5% of the signs were found correctly.

It must be again pointed out that the "product" function in fact gives the "square of the structure" and not the structure as such, so that here, as in a number of other relationships used in direct methods, what is really determined is the sign (phase) of the structure amplitude of the "square" of the structure and not of the structure itself.

Vaughan [49] obtained relationships of more general type, which do not require preliminary determination of the coordinates of at least one atom. He considered the generalized Patterson function

$$D_n(u_1, u_2, \ldots, u_n) = \int \rho(r)\rho(r + u_1)\rho(r + u_2)\ldots\rho(r + u_n)\,dv, \quad (15)$$

and a modified product function

$$Q_n(u_1 u_2 \ldots u_n) \prod_{j=1}^{n} I(u_j) \prod_{k<j} I'(u_j - u_k). \quad (16)$$

which are similar to each other when n = 2. Equating them,

$$D_2 = Q_2, \quad (17)$$

we obtain a formula connecting the structure product and intensities:

$$\varepsilon_{H_1}\varepsilon_{H_2}\varepsilon_{H_1+H_2} \sum_{j=1}^{N} g_j^2 \approx \approx A\sqrt{(\varepsilon^2_{H_1+K} - 1 + B)(\varepsilon^2_{H_2-K} - 1 + B)(\varepsilon^2_K - 1 + B)^K} - AB^2, \quad (18)$$

which includes the so-called normalized structure factors ε. Subtraction of certain quantities from both parts of the formulas and introduction of the coefficients A and B is associated with removal of zero peaks of the functions and with normalization.

Karle and Hauptman [50], who used a different approach, obtained more general formulas of the same type, which give not only the value of the structure product but also other relationships for special combinations of structure amplitudes and their moduli. These authors consider the joint probability distribution of certain normalized structure amplitudes, so that the structure is fixed and the indices vary continuously but not independently.

Let us consider this method with the example of the structure product. We choose two points H_1 and H_2 of the reciprocal lattice, and then form for each point K the product of three structure factors $\bar{F}_K \bar{F}_{H_1+K} \bar{F}_{H_2+K}$. This gives

rise to several hundreds or thousands of quantities (according to the number of reflections measured), and we are justified in raising the question of their distribution law. This law can be calculated by methods of the probability theory, and the required relationships are thus found.

The intensities are transformed into moduli of the normalized structure factors $|\epsilon|$ or their squares. Further, the formulas

$$\mu_p = \langle |\varepsilon_h|^p \rangle_k,$$
$$\lambda_{ph} = |\varepsilon_h|^p - \mu_p,$$
$$M_t = \left\langle \frac{|\varepsilon_k|^t - 1}{\log |\varepsilon_k|} \right\rangle_k, \tag{19}$$
$$\Lambda_{th} = \frac{|\varepsilon_h|^t - 1}{\log |\varepsilon_h|} - M_t,$$

are used to find the values of Λ. It is important to note that subtraction of M_t makes many of these Λ negative. The formulas connecting ϵ'' or the structure product with the triple convolution of the values of Λ have the following form:

$$\varepsilon''_h = 1 + \frac{2\sigma_2^2}{C_1^2(t)\,\sigma_4} \langle \Lambda_{tk} \Lambda_{t(h+k)} \rangle_k + R''_{2,0}. \tag{20}$$

$$\varepsilon'_{h_1} \varepsilon'_{h_2} \varepsilon'_{h_1+h_2} = \frac{\sigma_2^2}{C_1^2(t)\,\sigma_4^{1/2}} \langle \Lambda_{tk} \Lambda_{t(h_1+k)} \Lambda_{t(h_1+h_2+k)} \rangle_k -$$
$$- 2\frac{\sigma_2}{\sigma_4^{1/2}} + \frac{\sigma_2^{1/2}}{\sigma_4} (\varepsilon'_{h_1} \varepsilon''_{h_2} + \varepsilon'_{h_2} \varepsilon''_{h_1} + \varepsilon'_{h_1+h_2} \varepsilon''_{h_1+h_2}) + R''_{2,0}. \tag{21}$$

In Eqs. (19)-(21) the normalized structure amplitude $\varepsilon_h = I / \sigma_2^{1/2} \sum_{j=1}^{N'} f_j \exp(2\pi i \mathbf{h}\mathbf{r}_j)$; analogously, the normalized ε'_h of the square of the structure is determined through f_j^2 and σ_4, and the normalized structure amplitude ε''_h of its fourth power is found through f_j^4 and σ_8; here $\sigma_n = \sum_{j=1}^{N'} f_j^n$. $C_n t$ – is a tabulated function, with the optimum value of the integral parameter $t = 2$, $C_1(2) = 1.72$; R represents the remaining terms which may be neglected.

Karle and Hauptman also give a number of other formulas connecting structure amplitudes of their powers.

It should be noted that the Karle–Hauptman relationships give normalized structure amplitudes ϵ' of the square of the structure and not of the structure itself. Thus, if the signs of the structure itself and the square of the structure do not coincide, error will occur. Moreover, in the right-hand side of the equation we see the products of the structure amplitudes of the same reflection from the squared structure ϵ' and the fourth-power structure ϵ''. Evidently this comment is of no significance in relation to structures of like atoms. Equation (21) shows that the averaged triple product must be calculated as many times as there are nonzero reflections.

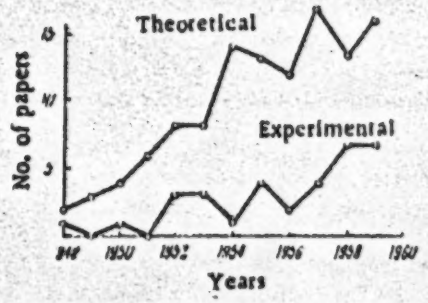

Fig. 14. Numbers of publications concerned with direct methods in different years (Journals: Acta crystallographica, Kristallografiya, Trudy Instituta Kristallografii, and Zeitschrift fur Kristallographie). The total number of publications through 1959 is 105 theoretical and 35 experimental papers.

Calculations with these formulas are extremely cumbersome and they can be used only by programming a computer.

The formulas which we are discussing are also valid for noncentrosymmetric crystals. In principle they can be used for phase determination. However, the formulas must first be tested out thoroughly for centrosymmetric crystals.

Equations (20) and (21) were tested by Silant'eva ans Stasova in the Institute of Crystallography of the Academy of Sciences of the USSR for a number of reflections of the above-mentioned astrakhanite structure, which is known

and which contains 34 atoms in the cell. The value of t was taken as 2. The results of tests of Eq. (20) and the fundamental Eq. (21) for certain structure products and signs found from them are given below:

Values of $|\epsilon'_h|$ from Formula (20)

hkl	$\lvert\epsilon'_h\rvert$ from (20)	ϵ'_h from structure data
400	2,94	— 2,77
140	2,50	— 2,10
540	2,96	+ 2,45
250	0,20	+0,283

Values of ϵ'_h from Formula (21)

Structure product	hkl	ϵ'_h from (21)	ϵ'_h from structure data
$\epsilon_{080}\epsilon_{140}\epsilon_{140} \approx -\epsilon_{080}\epsilon_{140}$	080	—1,42	—1,17
$\epsilon_{080}\epsilon_{040}\epsilon_{040}$	080	—0,4	—1,17
$\epsilon_{400}\epsilon_{200}\epsilon_{200}$	400	—2,6	—2,77
$\epsilon_{730}\epsilon_{400}\epsilon_{330}$	730	+1,9	+2,50

It is seen that the signs were determined correctly. What is especially valuable is that the sign of the 080 reflection in the second example, when the structure product is negative, is correctly determined. Karle [51] reported on the successful application of Eq. (21) to the structure of benzyldihydronicotinamide $C_6H_5CH_2(C_5H_6N)CONH_2$. Thus, these formulas give correct results for fairly complex structures and for not very strong structure products. It is obvious that more complete verification is needed for final assessment of their applicability. It should be noted that such an eminent specialist in the field of direct methods as Bertaut pointed out during discussions in Cambridge that the residual term R in these formulas may be of very great significance, distorting the result. In any event, the new equations of Karle and Hauptman must be tested for a number of structures.

8. Conclusion

Crystallographers all over the world have worked on the theory and practice of direct methods, and the present authors were unable to refer to the valuable contributions made by many of them in this fascinating field. One general feature attracted our attention: the number of theoretical papers has persistently exceeded the number of experimental structural determinations (Fig. 14). It is to be expected that there will be a break in the near future, and the number of experimental investigations by direct methods will rise sharply.

We consider that direct methods of analysis should receive more attention than they have done so far. We must emphasize once again that for not very complex structures with 25-30 like atoms in the cell the use of direct methods in the simplest form has a good chance of success. In such cases there is a certain number of reliable connections between the structure amplitudes. The signs of the remaining (weaker) amplitudes are determined statistically by Zachariasen's method.

The latest successes in the development of direct methods inspire great hopes. It is to be expected that they will become applicable to structures with 100-200 like atoms in the cell. Models are not needed for work by direct methods; such work is "linear" and can be entirely entrusted to a computer. As soon as this has been done, the question of automatic structure analysis will arise. The measured intensities could be fed directly into the computer, which would apply all the necessary corrections, calculate the absolute or normalized structure amplitudes, determine the signs of the amplitudes, compute the electron density series, and produce the final result.

It may be that many will then look back with regret on the interesting past, involving fascinating work on structure interpretation. However, development of direct methods of structure analysis promises to give us time for work which is no less fascinating – deeper studies of the chemical structure of molecules, crystal chemistry, and solid-state physics.

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PROBLEMS OF STRUCTURAL CHEMISTRY AT THE RIGA CONFERENCE

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Translated from Zhurnal Strukturnoi Khimii, Vol. 2, No. 5,
pp. 640-641, September-October, 1961
Original article submitted May 20, 1961

A conference on the theory of chemical structure, kinetics, and reactivity, convened by the Riga Polytechnic Institute, the Academy of Sciences of the Latvian SSR, and the Latvian Republican Division of the D. I. Mendeleev All-Union Chemical Society was held in Riga from May 8 to 13. The conference aroused great interest among chemists, as is shown by the fact that more than 500 people took part. There were two plenary sessions and four sections, each consisting of eight sessions, at which more than 200 papers were presented.

In this short communication it is impossible to refer to all the papers, or even to consider in the most concise form the main trends of the investigations reported at the conference. We must therefore confine ourselves to a very brief review of certain trends of research reported at the conference, concerned mainly with problems of molecular structure.

Mention must first be made of the paper by Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin, entitled, "Applicability boundaries of the electronegativity concept," presented at the final plenary session, which aroused great interest. The author showed, by means of extensive factual data, that the rapid development of physical methods of investigation, giving increasingly deeper insight into the subtleties of molecular structure, leads to a reappraisal of the fundamental concepts of the theory of the chemical bond. In particular, the concept of electronegativity, which has been in existence for over 20 years, and which is used by chemists to represent the ability of an atom in a molecule to attract electrons, is proving to be inadequate. This concept should reflect the asymmetry of the electron cloud of an atom in a molecule, which arises in the formation of a chemical bond. During recent years new factors have been discovered in assessment of chemical bond types: electron hybridization in the atom, the role of vacant orbitals and unshared electron pairs in formation of chemical bonds, dative bonds and bonds of the type existing in π-complexes, participation of free d-orbitals in bond formation, and formation of multicentered orbitals. The electronegativity concept does not take account of the influence of these factors. During the time since the origin of the electronegativity concept, new methods of quantum-mechanical calculation have been developed whereby effective bond charges can be estimated. Physical methods such as nuclear quadrupole resonance and x-ray spectroscopy have been developed; these make it possible to investigate molecular structure in much finer detail. The electronegativity concept is too narrow to reflect new facts and effects discovered by means of the latest physical research methods. The speaker demonstrated by means of numerous factual examples that the experimental and theoretical material which has accumulated in modern chemistry insistently demands the replacement of the obsolete electronegativity concept by new concepts which correspond to the modern level of development of the theory of the chemical bond.

Several communications concerned with various aspects of the chemical structure of molecules were presented at the sectional meetings.

The paper by M. E. Dyatkina and M. E. Shustorovich dealt with the topical problem of the electronic structure of aromatic metal complexes. Data obtained by calculation of molecular orbitals with self-consistency for the complexes $V(C_5H_5)_2$, $Cr(C_5H_5)_2$, $Fe(C_5H_5)_2^+$, $Co(C_5H_5)_2$, $Co(C_5H_5)_2^+$, $Ni(C_5H_5)_2^+$ and also $Cr(C_6H_6)_2$ and $Cr(C_6H_6)_2^+$ were used for explaining a number of properties of these compounds; in particular, their magnetic properties and electron paramagnetic resonance spectra, and the effective charges of the central atoms in complexes were calculated. The data were used for explaining differences in the ionic character of the complexes, the aromatic character of the rings, the relative stabilities of complexes, and certain other properties. The results obtained were used to explain the structure and properties of carbonyls of the transition metals and of their complexes with various organic ligands containing π-bonds.

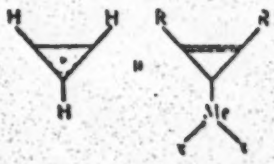
The paper by E. A. Shugam and L. M. Shkol'nikova, entitled "Structure of complexes and mechanism of the interaction of acetylacetone with transition metals," reported the determination of the crystalline and molecular structures of copper, chromium, cobalt, and aluminum acetylacetonates by the x-ray diffraction method. It was shown that the copper acetylacetonate molecule is planar, whereas the molecules of trivalent-metal acetonates have octahedral structure (with three acetylacetone groups in three mutually perpendicular planes). From the interatomic distances determined in these compounds it was found that the bonds formed by the metal atom with the ligand are equivalent, and that all the six-membered acetylacetone rings have "benzenoid" structure regardless of the nature of the metal atom.

A. F. Ievin'sh, Ya. K. Ozols, and S. G. Vimba determined the structure of rubidium tetraphenylboronate by x-ray structure analysis. The space group is $D_{2d}^{11} - \overline{I}42m$. The unit cell dimensions are a = 11.23 A, c = 8.09 A. The unit cell contains two molecules. The atomic coordinates were determined from projections. The boron atom is surrounded by four carbon atoms forming a regular tetrahedron. The rubidium atom is surrounded by four phenyl groups. The distances between the atoms in the tetrahedron are: B – C = 1.62 A; C – C = 2.65 A; the average Rb–C distance is 3.41 A.

Several papers by various authors were concerned with certain aspects of the structure and reactivity of compounds containing three-membered carbon rings (B. A. Kazanskii and M. E. Lukina: "Conjugation of a three-membered carbon ring with unsaturated groups"; M. E. Vol'pin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov: "Three-membered nonbenzenoid aromatic systems"; R. Ya. Levina, V. N. Kostin, P. A. Gembitskii, and S. M. Shostakovskii: "Conjugation in a system consisting of an aromatic and a trimethylene ring.")

B. A. Kazanskii and M. Yu. Lukina used a large number of examples for studying the hydrogenation, in presence of palladium, of a number of compounds of the cyclopropane series containing unsaturated groups adjacent to three-membered rings. It was shown that the degree of conjugation is influenced by the steric factor; this is in good agreement with theoretical views on the structure of the three-membered ring.

M. E. Vol'pin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov developed methods for synthesis of simple nonbenzenoid aromatic systems:



R. Ya. Levina, V. N. Kostin, P. A. Gembitskii, and S. M. Shostakovskii showed that introduction of an electrophilic substituent at the ortho and para positions to the three-membered ring leads to increase of conjugation between this ring and the benzene ring. A methyl group in the meta position has virtually no effect on this conjugation. In presence of two methyl groups in the ortho position to the cyclopropyl group the conjugation effect is completely removed by steric factors. The authors' analysis of interatomic distances shows that the molecular conformation favoring conjugation is forbidden in this case owing to steric hindrance. This conjugation effect is manifested in the chemical properties of aryl cyclopropanes.

The paper by M. G. Gonikberg and B. S. El'yanov was concerned with the very interesting problem of steric hindrance to chemical reactions. They estimated the steric difficulty of an elementary chemical step from the extent of the volume decrease in the formation of an activated complex. Such estimation makes it possible to separate experimentally the influence of spatial and polar factors on reaction rates. The volume decrease in the formation of an activated complex may be determined experimentally by studies of the influence of pressure on the reaction-rate constant. The steric hindrance characteristics for certain Menshutkin reactions, determined by this method, were given in the paper.

The communications mentioned above are by no means all the papers concerned in one way or another with problems of molecular structure. In particular, there was a whole series of papers on the use of many new physical methods for investigating fine structural details in chemical compounds (papers on the use of nuclear magnetic resonance, dipole moments, studies of the relationship between structure and photoconduction of certain substances, etc.).

The conference was very interesting and useful and was conducted at a high level. The conference organization was irreproachable. By the start of the conference the summaries of the papers had been published, and some of the papers were available in full (work of the Riga chemists of Academician G. Ya. Vanaga's school in the field of cyclic β-diketones). The other papers presented at the conference are also to be published in full.

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COMMISSION ON CRYSTAL STRUCTURE DATA

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

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Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
Life Sciences		Doklady Biological Sciences Sections (includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Doklady Botanical Sciences Sections (includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
Earth Sciences		Doklady Earth Sciences Sections (includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1 6	1957-1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1 6	1957-1958
Mathematics		Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
Physics		Soviet Physics–Doklady (includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
Élektrosvyaz	Élektrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). obozr(enie)	Entomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

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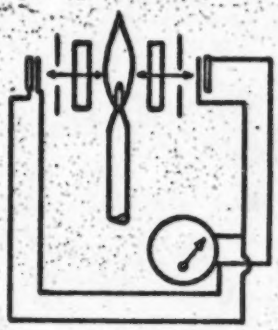
continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1 1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1 1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1 1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (in English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48 1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4 1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1 1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1 1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1 1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal tekhnicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.



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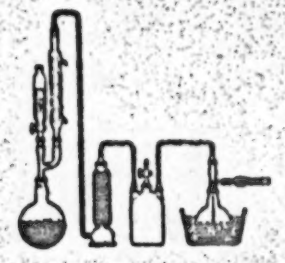

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